



# Journal of the Society of Chemical Industry.

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No. 12, Vol. XXXIV.

THE SOCIETY OF CHEMICAL INDUSTRY.

## INCOME AND EXPENDITURE ACCOUNT FOR YEAR ENDING 31st DECEMBER, 1914.

EXPENDITURE.				INCOME.			
	£	s.	d.		£	s.	d.
10 Journal—Editorial and Sundry expenses—				By Entrance Fees .....			164 17 0
Editor's Salary .....	542	16	0	Life Composition Fees .....			37 10 0
Do. Expenses .....	32	11	3	Annual Subscriptions .....	318	4	10
Do. Assistant .....	156	0	0	Journal Advertisements .....			4852 15 0
Abstractors .....	628	8	9	Sales .....			885 4 10
Sub-Editor's Salary .....	150	0	0	Collective Index—Subscriptions ..			1203 9 8
Indexing Journals, &c. ....	131	6	0	Decennial Index—Sales .....			12 10 0
Foreign Journals, &c. ....	30	18	4	Dividends and Interest on Invest-			
Sundry Journals .....	2	11	9	ments—			
French and U.S.A. Patents and				£	s.	d.	
Specifications .....	42	1	9	4476	8	2	Metropolitan 3%
Insurance of Stock .....	6	18	0	Consolidated .....	126	0	10
				1000	0	0	New Zealand 3%
Publishing expenses—				(1945) .....	28	3	9
General .....	1807	3	6	1277	4	8	New South Wales
Postage on Copies 741 12 0				3% (1925) .....	36	0	1
	2548	15	6	1231	0	10	Consols 2½%
				600	0	0	Gas Light and Coke
Sectional expenses—				3% Debentures .....	16	18	3
Boston .....	19	0	0	1084	13	4	North British 3%
Birmingham and Midland ..	42	4	2	3% Consolidated ..	30	11	7
Canada .....	12	3	7	1626	0	0	Molten (Rly.) 2½%
Liverpool .....	85	14	3	1500	0	0	Great Eastern Rly.
London .....	101	17	3	4% Irredeemable ..	56	15	5
Manchester .....	83	2	11	678	0	0	South Eastern Rly.
Newcastle-on-Tyne .....	0	10	0	4½% Preference ..	28	0	1
New York .....	100	0	0	1000	0	0	Metropolitan Water
Nottingham .....	26	19	4	Board 3%, "B" ..	28	3	9
Scotland .....	15	15	0	Debentures .....			
Sydney .....	16	16	1	200	0	0	Nottingham Joint
Yorkshire .....	23	1	4	Station 3% .....	5	12	11
Annual Meeting expenses .....				1250	0	0	Great Western Rly.
Working expenses—				5% Guaranteed ..	58	15	10
Secretary's Salary .....	300	0	0	800	0	0	Great Northrn Rly.
Assistant to Secretary and				3% Debentures ..	22	11	6
Editor .....	250	0	0	450	0	0	Nottingham and
Honorary Treasurer's				Grantham Canal			
Assistant and for Clerical				4½% Consolidated ..	17	5	5
Assistance .....	77	10	0	724	8	0	India 3½%
Print, Lighting and Cleaning	208	9	1	834	0	2	India 3%
Stationery and Binding .....	50	10	0	1100	0	0	Dominion of Canada
Postages, Bank Charges, Tele-				Canadian Pacific			
phone and Sundry expenses	167	14	0	Rly. 3½% Land			
Medallist Portrait .....	31	5	6	Grant Bonds 1888			
				700	0	0	Canada 4% (1940—
				1900) .....	26	6	2
				703	8	5	Western Australian
				Government 4% ..	13	2	7
Excess of Income over Expenditure				Interest on Deposit ..	36	3	0
							603 0 4
							£6071 1 0
	£6071	1	0				

### Manchester Section.

Meeting held at the Grand Hotel on Friday, January 8th, 1915.

MR. JULIUS HUBNER IN THE CHAIR.

#### AN IMPROVED METHOD FOR THE DETECTION OF COBALT BY MEANS OF $\alpha$ -NITROSO- $\beta$ -NAPHTHOL.

By F. W. ATTACK, M.Sc. TECH., B.Sc. LOND., A.I.C.

The use of  $\alpha$ -nitroso- $\beta$ -naphthol ( $\beta$ -naphthoquinone- $\alpha$  oxime) in alcohol or acetic acid solution as a reagent for cobalt was first suggested by Hlinski and Knorre (Ber., 1885, 18, 699). The cobalt compound so obtained is somewhat soluble in alcohol and in acetic acid, and the test does not appear to be one of great delicacy compared with the reagents for nickel which have been suggested by Tschugaeff (Ber., 1905, 38, 2520)

and by Attack (Analyst, 1913, 38, 316). The exact composition of the reagent to be used is not stated by Hlinski and Knorre, but Chapin (J. Amer. Chem. Soc., 1907, 29, 1023) suggests the use of a solution of 8 grms. of  $\alpha$ -nitro- $\beta$ -naphthol in 300 c.c. of cold glacial acetic acid, to which an equal volume of water is added, and the solution filtered. It is stated that the solution cannot be preserved for more than one month; the present author has found that the nitrosonaphthol is gradually precipitated from the 50% acetic acid solution. Using this solution it was found impossible to detect with certainty less than 0.1 mgrm. of cobalt in 1 c.c. of water (1:10,000) in presence of several drops of dilute hydrochloric acid. No mention is made by Chapin of the delicacy of the test, but the smallest amount of cobalt detected by Hlinski and Knorre (*loc. cit.*) appears to have been 0.00004 grm. in presence of 0.0105 grm. of nickel in 5 c.c. of water (1 part of cobalt in 100,000 parts of water). In presence of large amounts of nickel, the author has found it impossible to prevent the precipitation of the nickel salt, which masks the cobalt color-

## THE SOCIETY OF CHEMICAL INDUSTRY.

## BALANCE SHEET, 31st DECEMBER, 1914.

	£	s.	d.	£	s.	d.		£	s.	d.	£	s.	d.
By Sundry Creditors .....				745	15		By Sundry Debtors (Publishers &c.) ..				461	18	0
.. Subscriptions received in advance				61	4	0	.. Arrears of Subscriptions (received up to 31st April, 1915) .....				34	0	0
.. Accumulated Fund—							.. Cash at Bank on Deposit .....	400	0	0			
Balance 31st December, 1913 ..	20,344	4	7				.. Do. do. Current Account .....	138	4	3			
Add—Excess of Income over Expenditure, 1914 .....	891	15	2	21,238	19	0	.. Cash in hand (Secretary) .....	9	17	7	548	1	0
							.. Investments as last year—						
							£	s.	d.				
							4476	9	2	Metropolitan 3%	1163	4	1
							1000	0	0	Consolidated .....			
							1277	4	8	New Zealand 3% (1915) ..	870	0	0
							1231	0	10	New South Wales 3% (1915) ..	1122	3	1
							600	0	0	Consols 2½% .....	1031	15	4
							1081	13	4	Gas Light and Coke Co. 3% Debentures ..	507	0	0
							736	0	0	North British 3% Consolidated .....	900	5	6
							969	0	0	Midland Ry. 2½% Perpetual .....	1187	4	0
							1509	0	0	Guaranteed Preference .....			
							673	0	0	Great Eastern Ry. 4% Irredeemable ..	1620	14	5
							1000	0	0	South Eastern Ry. 4½% Preference ..	747	0	7
							200	0	0	Metropolitan Water Board 3% "B" Debentures .....	422	10	0
							1250	0	0	Notttingham Joint Station 3% .....	166	0	0
							800	0	0	Great Western Ry. 3% Guaranteed ..	1762	10	0
							450	0	0	Great Northern Ry. 3% Debentures ..	606	0	0
							724	8	0	Notttingham and Grantham Canal 4½% Consolidated ..	495	0	0
							834	0	2	India 3½% .....	700	0	0
							1400	0	0	Bonds 1938 .....	700	0	0
										Dominion of Canada (Canadian Pacific 3½% Land Grant Bonds 1938) .....	1572	4	0
										Canada 1% (1910-1960) .....	676	8	1
											19,648	17	1
							Add—Purchased during 1914						
							703	8	0	West Australian Government 4% ..	698	3	0
							700	0	0	War Loan 3½% ..	661	0	2
											21,008	0	3
											£22,056	0	1

\* Market value on Dec. 31st, 1914, £18,693 4 2

We have examined the above Balance Sheet, dated 31st December, 1914, and have verified the investments and the balances at the Bank. In our opinion the Balance Sheet shows correctly the position of the Society at 31st December, 1914.

28, Basinghall Street, London, E.C.

28th April, 1915.

(Signed) FLEASKEY &amp; CO.,

Chartered Accountants.

tion, even by the addition of a considerable amount of hydrochloric acid, which is stated by Chapin to decrease considerably the delicacy of the test. Moreover, the addition of the reagent to water alone produces a heavy yellow to brown precipitate. It appeared to the author that a more stable solution of this oxime would be obtained in the form of its sodium salt, which, according to Ilinski and Knorre (*loc. cit.*), gives on addition to a solution containing cobalt a salt in which the cobalt is only divalent. It has been found that such a solution provides a far more delicate test for cobalt than the acetic acid solution of the reagent. The solution recommended for use is much more dilute, a reagent of a convenient

strength for general use being prepared as follows: 0.1 gram of  $\alpha$ -nitroso- $\beta$ -naphthol is boiled with 20 c.c. of water to which has been added 1 c.c. of dilute caustic soda, the solution filtered, and diluted to 200 c.c. A sample of the reagent has been preserved for a year, and there does not appear to be any reason to suppose that it cannot be kept indefinitely. In carrying out the test 1 c.c. of ammonium chloride and then 1 c.c. of the reagent are added to the neutral or slightly alkaline solution under examination. The production of an orange to claret coloration, or a red precipitate, unaffected by acidifying with dilute sulphuric acid, is characteristic of the presence of cobalt. 0.001 mgrm. of cobalt in

1 c.c. of water, or 1 part of cobalt in a million parts of water, may be detected readily by the test as now described, this amount giving immediately a claret coloration, and a slight red precipitate on allowing to stand. This method of carrying out the test with the sodium salt is hence far more delicate than the method originally proposed and now in general use; the test may be made even more delicate by using the reagent of one-fifth the concentration recommended above for general use, and comparing the test with a "blank." The colorations obtained with nickel, ferric, etc., salts are all destroyed on acidifying with sulphuric acid. It is immaterial whether the cobalt is present in the solution as nitrate or other salt, provided that it is in the cobaltous condition, whereas Ilinski and Knorre (*loc. cit.*) state that it is necessary to have the cobalt present as chloride or sulphate in order that their method shall succeed.

The test is not affected by the presence of zinc or manganese salts in the solution. The presence of large amounts of nickel interferes with the intensity of the coloration, although it does not prevent the detection of the cobalt, a yellow coloration, and eventually a red precipitate, being obtained with a solution of a sample of nickel ammonium sulphate which contained cobalt, whereas solutions of samples of nickel nitrate and nickel chloride, containing the same concentration of nickel but free from cobalt, gave green solutions on acidifying the test solution with sulphuric acid. For the detection of cobalt in presence of large quantities of nickel, it is advisable to reduce the concentration of the nickel by precipitation with an alcoholic solution of dimethylglyoxime (Tschugaev, *loc. cit.*) or  $\alpha$ -benzildioxime (Atack, *loc. cit.*). As the presence of either of these nickel reagents in excess gives rise to a cobalt salt which will not react with the nitroso-naphthol reagent, it is essential to separate the nickel partially only.

It is to be noted that this interference with the test by large amounts of nickel is an advantage in general analysis, as the amounts of cobalt present in commercially pure nickel salts do not give a precipitate, but only a coloration, with the new reagent at the concentrations usually employed in qualitative analysis, whereas such amounts are sufficient to give the test with the acetic acid solution in such a manner that, as Chapin remarks (*loc. cit.*), students report cobalt as present in every solution of nickel which they analyse.

The test is not affected by the presence of tartaric or citric acid, which may therefore be employed to keep in solution members of Group III. of the analytical classification: in this manner 0.001 mgrm. of cobalt was readily detected in presence of 1 mgrm. of iron (as ferric ammonium citrate).

The quantitative application of the method is under examination.

Meeting held at the Grand Hotel on Friday, April 9th, 1915.

DR. JULIUS HURNER IN THE CHAIR.

#### THE CONSTANTS OF THE FATTY ACIDS FROM SULPHONATED COD OIL.

BY L. G. RADCLIFFE AND C. W. PALMER.

It is well known that all saponifiable oils can be sulphonated with considerable ease and completeness; moreover, the process is largely carried out on the cheaper oils. A sulphonated oil has properties and constants which differ entirely

from the original oil, and it is therefore extremely difficult to identify an oil after it has been sulphonated.

It has been thought useful to sulphonate certain oils and then to hydrolyse the sulphonated product so as to remove completely the sulphonic groups and finally to prepare the fatty acids therefrom and compare their properties with those of the fatty acids from the unsulphonated oil, in the hope that the figures so obtained would prove of use in the analysis and identification of the original oil.

The cod oil used was a brown variety, having a sp. gr. of 0.931 at 15.5°C.; saponification value, 163.3; acid value, 17.6, corresponding to 8.9% of free fatty acid calculated as oleic acid; iodine value, 173.7%.

From this oil the free fatty acids were prepared by saponifying with strong potash and alcohol; the soap was boiled with water to remove the alcohol and the fatty acids precipitated by hydrochloric acid. The clear oil was well washed with water, separated, and heated until free from moisture. The fatty acids had a solidifying point (titer test), 22.8°C.; neutralisation value, 194; mean molecular weight, 280.1; iodine value, 178%; yield of hexabromides, 42%. The sulphonation was performed on 100 grms. of the oil in a suitable vessel cooled with a water-jacket and provided with a thermometer and a mechanical agitator driven by a hot air motor. To the oil 35 grms. of concentrated sulphuric acid was added drop by drop from a tap funnel and the reaction was carefully controlled so that the temperature did not at any time rise above 25°C.; no production of sulphur dioxide was noticed. After two hours stirring no further action was observed, and the darkened and thickened solution was washed with a cold saturated solution of sodium sulphate until nearly all the free sulphuric acid was removed. The product dissolved in dilute ammonia to a clear solution. On heating the sulphonated oil in the water-oven a clear oil was obtained, and from this the fatty acids were prepared.

The sulphonated oil was saponified with aqueous caustic potash and alcohol in the same way as was the original oil, and after saponification the fatty acids were liberated as before, well washed, and dried in the water-oven. The clear oily fatty acids were tested for sulphur with negative results. These acids were of much harder consistency than the acids from the unsulphonated oil and on examination gave the following data: Solidifying point (titer test), 25.7°C.; neutralisation value, 187; mean molecular weight, 308.6; iodine value, 111.1%. These figures indicate a very extensive alteration in the chemical constitution of the fatty acids regenerated from the sulphonated oil as compared with those of the original cod oil.

The behaviour of other oils is being investigated and the further results will be communicated in a later paper.

#### DISCUSSION.

Mr. J. ALLEN said that the so-called commercial cod oils were mixtures of oils obtained from all kinds of fish, and usually of a dark brown colour, and in an advanced state of decomposition. Such oils were obtained not only from the liver of the fish but also from the entrails. Hence their characteristics were extremely variable. It was, therefore, difficult to understand how the authors could hope to find any means of establishing the origin of sulphonated oils which were of such diverse origin. The treatment of fatty glycerides with sulphuric acid inevitably resulted in the formation of hydroxy acids or stearolactones; the determination of the acetyl value of the oil before and after sulphonation, thus measuring

the extent of the introduction of hydroxyl groups into the molecules of the fatty acids, would, therefore, be likely to throw further light on the changes taking place on treating the oil with sulphuric acid.

Mr. L. E. VILES thought that 8.9% of free acids was high and that the authors must have been working with "coast cod oil." In his experience maximum sulphonation would not be obtained with ordinary sulphuric acid under the conditions indicated; a longer action and the use of monohydrate being necessary. The power of the sulphonated product to emulsify mineral oil was a useful guide as to the progress of the sulphonation. The sulphonated, or more correctly sulphated, oil was easily hydrolysed by boiling with dilute mineral acid. He asked the authors if they had definitely established that the products of hydrolysis were hydroxylated compounds.

The CHAIRMAN asked whether it could be ascertained what kind of oil or what mixture of oils had been used in the manufacture of a Turkey-red oil. He noted that the fatty acid was different when recovered from the sulphonated oil. That seemed to be borne out by the fact that in dyeing, different shades were produced with different oils.

Mr. F. H. TERLESKI said that coast cod oil sometimes contained 50% of hydrocarbons. Mr. Viles had stated that 8% of free fatty acids was rather high, but it was quite common to get as high a figure as 80% on the saponifiable matter.

Mr. RADCLIFFE said that he had carried out a considerable amount of research with regard to the acetylation value, and hoped to be able to communicate the results later. The present work had not been carried out with a view to identifying particular cod oils, so that it was immaterial for his purpose whether the oil was adulterated. In reply to Mr. Viles, the sulphonic group could be eliminated partly by steam and completely by using dilute sulphuric or hydrochloric acid. So far as he had been able to observe, the products appeared to be hydroxyl compounds. He did not know of any method which would identify the original oils in a sulphonated mixture of oils.

#### THE METAL CONTENT OF SOME LINOLEATES AND ROSINATES.

BY L. G. RADCLIFFE AND C. W. PALMER.

A number of so-called rosinates and linoleates are now offered for various purposes in connection with paints and varnishes, and these are usually made either by fusing an oxide of the metal with rosin, or by saponifying rosin with caustic soda or sodium carbonate, care being taken to avoid an excess of alkali, and then adding a solution of a metallic salt, generally the sulphate or the chloride. The precipitated rosinato, resinate, or sylvinate, as it is variously called, is then washed with water, pressed, and dried.

The precipitated rosinates contain varying percentages of water, whilst those produced by the fusion method are anhydrous. Common rosin or colophony consists almost entirely of abietic acid, and although the metallic salts of this acid are much used in the lacquer and varnish industry as driers and to make substitutes for hard resins, little definite information has been published in regard to their chemical composition. Abietic acid, according to Maly, exists in rosin as the anhydride, but this view is discredited by the ease with which rosin in alcoholic solution can be titrated with alkalis. Arch has isolated a form of abietic acid by extracting rosin with 70% alcohol and then repeatedly recrystallising the product from 90% alcohol. The acid which he obtained was white, but melted indefinitely from

148° to 154° C.; he suggested for it the formula,  $C_{19}H_{28}O_2$ , and this was supported by Tschirch and Studer (Arch. Pharm., 1903, 241, 495). Fahlén obtained a similar acid from American rosin and called it sylvic acid. Various investigators have studied this acid obtained from rosin and have given various formulae and melting points for it, but the work of Bischoff and Nastvogel, now generally accepted, appears to settle the formula as  $C_{20}H_{30}O_2$ . It is not necessary to discuss the work of Vesterberg, Haller, Jean, and others on pimaric acid.

Certain salts of abietic acid, described later, have been prepared in connection with a study of the relative efficiency of driers, and we are indebted to Dr. Knecht for a quantity of crystalline abietic acid prepared from French rosin. This acid melted between 149° and 156° C., and had a molecular weight of 304, corresponding to an acid  $C_{20}H_{30}O_2$ . Since abietic acid is monobasic, as shown by the presence of only one carboxyl group and the proportion of alkali required for its neutralisation, the composition of its metallic compounds can be represented by the formula  $(C_{20}H_{29}COO)_2 M$ , where M represents a divalent metal.

The salts with cobalt, lead, and manganese were prepared by dissolving the abietic acid in alcohol, carefully neutralising with an alcoholic solution of caustic potash, and evaporating the mixture to dryness; the potassium salt was dissolved in water and a solution of cobalt chloride, or manganese chloride, or lead acetate, added until no further precipitate was formed. The precipitate in the case of cobalt was dark heliotrope in colour, the manganese salt faint pink, and the lead salt white. The precipitates were filtered and thoroughly washed with cold water, dried on a porous tile, and then in a water oven until of constant weight.

The cobalt salt was analysed by igniting until free from carbon and then reducing the residual oxide in dry hydrogen and weighing as metal. Calculated for  $(C_{20}H_{29}O_2)_2 Co$ , the percentage of cobalt is 8.98; found 9.05% Co.

The manganese salt was ignited and the residue determined as  $Mn_2O_3$ . Calculated for  $(C_{20}H_{29}O_2)_2 Mn$ , the percentage of manganese is 8.3; found 8.5%.

The lead salt was ignited, the residue treated with strong nitric acid, then with strong sulphuric acid, and then weighed as lead sulphate. Calculated for  $(C_{20}H_{29}O_2)_2 Pb$ , the percentage of lead is 25.6; found 25.9%.

The linoleates are prepared from linseed oil by converting it into a soap and then adding a solution of the salt of the metal. It seems rational that such substances should be valued according to the content of metal and also that the loss, presumably of water, at 100–101° C., should be determined, in the case of the precipitated rosinates; therefore a number of commercial rosinates and linoleates have been examined and the results are recorded herewith.

It may be of interest to describe briefly the different salts and some of the uses for which they have been suggested. Precipitated rosinato of zinc is a fine white powder, and the fused form is in rosin-like lumps. Both are used to harden ordinary resin; the two are melted together at 180–190° C., and the product is used to make a cheap varnish. Precipitated rosinato of calcium is a white powder and the fused form is in lumps, as is always the case with the products made by the fusion method. It is used with rosin and linseed oil, giving a product which, when thinned with turpentine, is a form of resin lacquer.

Rosinate of copper has only been examined in the precipitated form; it is a fine green powder used for preparing anti-fouling marine paints, and also for wood impregnation.

Rosinate of magnesium is met with in both a precipitated and a fused form; they are practically colourless and are used in sealing wax compositions. They contain small quantities of iron, apparently as an accidental impurity.

Precipitated rosinate of manganese is an almost colourless powder, but the fused form is in dark, reddish-brown lumps. Both forms are important and efficient siccatives or driers, and usually about 2% dissolved in hot linseed oil is sufficient to produce an oil varnish, liquid driers, or the like. Rosinate of lead, in both forms, is also stated to be a very efficient drier, and it is used in about the same proportion and in the same way as the manganese salt.

Fused rosinate of cobalt is generally regarded as being the most efficient drier of the series, but it is rather expensive.

A mixed rosinate, containing both manganese and lead, is made in the fused and precipitated forms. Such a mixed salt is a very efficient drier, and it is stated that in order to obtain the best results the manganese and lead salts should be mixed in such proportions that the metallic lead and manganese, in the finished drier, should be as 5 to 1 respectively.

These rosins are soluble in linseed oil; the precipitated ones will generally dissolve in the cold oil, but the fused ones must be heated with the oil to about 120° C.; they are also soluble in turpentine. Several workers have examined commercial rosins; *vide* Amsel (*Z. angew. Chem.*, 1896, 9, 429), Meister (*Farbenzeit.*, 1907, 51, 1611), Hefelmann (*Chem. Rev. Fett-u. Harz-Ind.*, 1901, 8, 191).

TABLE I.  
*Metallic rosins.*

Name.	Percentage of metal.	Loss at 100° to 104° C.
Zinc, precipitated .....	7.7	4.7
Zinc, fused .....	3.6	Nil
Calcium, precipitated .....	4.6	5.3
Calcium, fused .....	3.0	Nil
Copper, precipitated .....	7.8	2.3
Magnesium, precipitated .....	5.1	7.2
Magnesium, fused .....	0.7	Nil
Manganese, precipitated .....	3.5	6.8
Manganese, fused .....	2.3	Nil
Lead, precipitated .....	12.2	9.5
Lead, fused .....	16.7	Nil
Cobalt, fused .....	2.4	Nil
	Mn	Pb.
Manganese-lead, precipitated ..	2.3	10.8
Manganese-lead, fused .....	1.13	7.2

Manganese oxalate has also been examined, as it is used as a drier; the sample was in the form of a slightly pink powder and contained 30.9% Mn. This salt is prepared by adding manganese chloride solution to a solution of neutral sodium or potassium oxalate.

The linoleates are the metallic salts of linseed oil fatty acids, and can be made by the precipitation method, though sometimes the mixed fatty acids are heated with the oxide of the metal. Tungates made from the fatty acids of tung oil are also in use, but these have not been examined.

Two commercial acids, known respectively as linoleic acid and tung acid, may be mentioned here. Linoleic acid, in the form of a thick, semi-thick yellow substance, has a characteristic odour; the acid value is 186.5 (corresponding to a mean molecular weight of 300 to 301), and the saponification value 202, i.e., 15.5 mgrms. of potash was used to saponify some unchanged oil. Tung acid was in the form of strongly smelling yellowish semi-solid lumps, having an acid value of 181, a mean molecular weight of 309 to 310, and a saponification value of 213; this again indicates

the presence of some unchanged tung oil. Both these acids are used in varnish making.

The following is a brief description of some of the linoleates and their uses.

Manganese linoleate is in the form of yellowish lumps and is used as a drier in varnish. Lead linoleate in the form of yellowish lumps is used for quick drying varnishes. Both of these can be dissolved in warm linseed oil, and mixtures of the two are frequently used.

Copper linoleate is in the form of dark green lumps and is used in anti-fouling paints.

Cobalt linoleate is in the form of dark maroon coloured rather soft lumps and is a very powerful drier.

Aluminium linoleate is a sticky mass and is used for waterproofing fabrics. The zinc, calcium, and magnesium linoleates have also been examined.

In all the analyses of the rosins and the linoleates the materials have been carefully incinerated and the residue suitably dissolved, and precautions taken to ensure the use of a method and precipitant which would effectually separate the metal from any other substances. In no case has the ash been taken as a criterion of the metal content.

TABLE 2.  
*Metallic linoleates.*

Name.	Percentage of metal.
Manganese .....	9.4
Lead .....	25.8
Copper .....	7.7
Aluminium .....	1.6
Cobalt .....	9.5
Zinc .....	9.0
Calcium .....	8.3
Magnesium .....	3.4

#### DISCUSSION.

Mr. J. ALLAN said that if it were possible to know the ratio of metal combined with an equivalent of the acid, say the abietic acid, and how much abietic acid was free in the mixture, a better comprehension of the combination of the materials mentioned would be obtained. The proportion of free and combined resin acids could be easily ascertained by determining the alkali saturation value and calculating how far the amount of lead found was in a definite ratio to the quantity of alkali taken up by the fatty acids.

#### Scottish Section.

Meeting held at Glasgow on Tuesday, 23rd February 1915.

MR. ROBERT HAMILTON IN THE CHAIR.

#### NOTES ON THE ANALYSIS OF GUARA AND GUARA EXTRACT.

BY THOMAS CALLAN, M.Sc., Ph.D.

Guara is a newly-introduced tanning material which, according to Eitner (*Gerber*, 1911, 40, 85-86) is identical with a material introduced 25 years ago under the name of Casarlotte. It was thought to be of interest to compare the material offered to British tanners as "guara" with the material described by Eitner. According to Eitner guara consists of the ground fruits of a variety of divi native to South and Central America, freed from seeds and woody husks. In agreement with this the samples of guara examined were found on microscopical examination to consist almost

wholly of fruit wall minus the outer husk. The most distinctive features in the microscopical appearance are the small brown plates showing a honeycomb structure and small brown plates furnished with stiff needle-shaped hairs, probably portions of outer epidermis and underlying tissue. According to Eitner (*loc. cit.*), guara contains a mixture of pyrogallol- and catechol-tannins, but practically all the reactions of guara tannin were found to agree with a pyrogallol-tannin closely resembling the tannins of sumach or myrobalans. Thus a dilute aqueous infusion of guara gives a violet-blue coloration with iron alum, no precipitate with bromine water, no phloroglucinol reaction with a deal shaving, a yellow precipitate turning green with lime water, a slight precipitate with formaldehyde and hydrochloric acid, a yellow coloration with sodium sulphite, an intense red or brownish-red coloration with an ammoniacal solution of potassium ferrieyanide in very dilute solution, a pink to purple coloration with Bennett's iodine test, and a deep orange-brown colour with nitrous acid. With concentrated sulphuric acid, however, a crimson-pink coloration changing to pink on dilution is obtained—a reaction given by most catechol-tannins.

A number of analyses of various samples of guara made during the past two years show that material of a remarkably constant quality is being supplied. The following are typical analyses, carried out according to the official method of the International Association of Leather Trades Chemists:—

	Tann.	Non-tann.	Insoluble.	Moisture.
	%	%	%	%
1.	45.5	23.8	22.0	10.5
2.	46.2	25.8	19.0	10.0
3.	44.1	29.2	17.7	10.7
4.	44.8	29.1	21.7	10.4

Mr. H. Lang, of the Gryfe Tannery, Ltd., kindly carried out for me a number of tanning experiments with guara and also made trials of this material on the large scale in conjunction with other tanning materials. According to these experiments, skins tanned entirely with guara gave a soft, well-filled leather, resembling a gambler tannage rather than a sumach or myrobalan tannage such as the presence of pyrogallol-tannins might lead one to expect. The well-nourished appearance of guara-tanned leather may therefore be largely due to the nature of the non-tannins present.

Guara is quite free from the liability to give excessive fermentation such as is characteristic of divi. However, its fine state of subdivision prevents guara from being readily leached, although the tanning matters are very readily soluble. Guara has been found excellent for developing acidity in the tan-liquors, and when used with untreated quebracho extract has a very favourable influence on the colour of the leather. It has been found particularly useful mixed with quebracho extract in the paddle, as it does not draw the grain but gives a soft and mellow tannage. The most characteristic features of guara are its acid-forming properties and the light colour and mellowness of the tannage.

*Guara extract.* Only one sample of guara extract (solid) has been examined, as this material is no longer imported.

The analysis gave tann., 41.7%; non-tann., 20.6%; insoluble, 11.0%; moisture, 17.3%, agreeing closely with the analysis given by Eitner. Guara extract gives a very dark coloured infusion

and besides being actually weaker in tannin, is inferior in all respects to the natural product. The large amount of insoluble matter makes its filtration during analysis very difficult. It is reported by Eitner to make a dark-coloured and unsatisfactory leather, and as it has not been favourably received by British tanners it is no longer imported.

#### NOTE ON THE ANALYSIS OF TANNING MATERIALS.

BY THOS. CALLAN, M.Sc., PH.D.

Whilst the experiments on guara described in the previous paper were in progress, there appeared a paper by H. G. Bennett (this J., 1914, 1182, 1184) in which a modified method of tannin analysis was proposed.

Briefly stated, Bennett proposes to modify the present official method of the International Association of Leather Trades Chemists by (1) exactly neutralising the hide powder before the preliminary chroming, (2) using less hide powder, (3) diluting the solution to be detannised with an equal volume of water, (4) using a more basic chromium salt for chroming. The object of these modifications is to obtain lower tannin results and higher non-tannins, this being a step towards greater accuracy, as the chief objection to the present method is that the hide powder absorbs small quantities of non-tannins as well as tannins. To test this new method analyses were made of guara using (1) the present official method with American hide-powder of standard quality, (2) Bennett's method using American standard hide-powder, (3) Bennett's method using finely ground hide-powder obtained from the Deutsche Versuchsanstalt für Lederindustrie, Freiberg. Using the same tannin solution, the amount of non-tannins obtained by these three methods were, to give only one example, 23.1%, 28.1%, and 25.1% respectively. Repeat experiments gave similar results.

In each case 50 c.c. of the detannised filtrate was tested by the official test for tannin (the addition, drop by drop of a 1% gelatin-10% salt solution) when no turbidity or opalescence was obtained, indicating apparent complete detannisation. This would indicate that the most accurate result was No. 2 showing the least absorption of non-tannins. The correctness of this reasoning, however, depends entirely on the trustworthiness of the official gelatin-salt test. The non-tannin filtrates were therefore re-tested by the tannin test devised by Stiasny, which consists of adding 1 c.c. of a saturated salt solution, then 2 drops of 1% metaphosphoric acid solution, and finally 2 drops of 5% gelatin-5% salt solution to 3 c.c. of the solution to be tested. With this more sensitive test No. 1 and No. 3 showed no tannin, whilst No. 2 showed a distinct trace. The dried non-tannin residues after weighing were therefore dissolved in 15 c.c. of warm distilled water, filtered and 3 c.c. tested by Stiasny's test. No. 1 gave no reaction, No. 2 gave a heavy precipitate, whilst No. 3 gave a distinct opalescence, indicating a slight trace of tannin. From these experiments with guara, which were repeated several times with similar results, the only method showing perfect detannisation is the present official process, although the amount of tannin remaining unabsorbed in Bennett's method when the finely ground Freiberg powder is used, is very small. Although the present official method undoubtedly detannises very completely, this does not mean that it is the more accurate, as these experiments do not show how much non-tannin is also absorbed. A number

of experiments were then made to determine the approximate degree of accuracy of the present official tannin test. With a solution of guara and also of chestnut extract it was found that 50 c.c. containing 10 mgrms. of tannin gave a distinct reaction, whilst 6.5 mgrms. in 50 c.c. could not be detected, although Stiasny's test readily showed as little as 3 mgrms. in 50 c.c. when only 3 c.c. of solution was taken for the test. With quebracho extract the official test is more delicate, indicating distinctly 5 mgrms. but not 2.5 mgrms. of tannin in 50 c.c. It follows, therefore, that a solution apparently completely detannised when tested by the official method may still contain, with some tanning materials, up to 6.5 mgrms. of tannin in 50 c.c. This would correspond in the case of a tanning material containing about 50% tannin to nearly 2% tannin, whilst with Bennett's method, owing to increased dilution, it corresponds to about double this amount. Before conclusions as to the relative efficiency of different methods of detannising tannin solutions can be drawn, it is therefore necessary that a more stringent test than the present official tannin test be used. A sufficiently stringent test would be to concentrate 6 c.c. of the presumably detannised solution (or 12 c.c. if Bennett's method or other method involving solutions more dilute than the present limits be used) to 3 c.c. and apply Stiasny's test.

In the course of a number of analyses of various tanning materials it was found, as in the case of guara, that the non-tannin filtrates obtained in Bennett's method, using standard American hide powder, showed in many, though not all, cases distinct traces of tannin, even after shaking 20 minutes with hide powder, when tested by the more sensitive method after concentration, although no tannin was shown by the official test. It would appear therefore that the alteration in the various factors in this method, designed to reduce absorption of non-tannins, has been carried too far, and although in all probability the gain in accuracy owing to reduced absorption of non-tans is more than the error introduced by the non-absorption of traces of tannin, the presence of this latter error will probably prove a strong objection to the method as it now stands.

In conclusion it may be noted that although Stiasny's test will give a positive reaction with gallic acid in sufficiently concentrated solution, it will not show 150 mgrms. of gallic acid in 50 c.c., which is about the maximum amount of gallic acid likely to be present in a detannised solution even after concentrating to half its volume.

### Sydney Section.

#### THERMO-REGULATOR FOR THERMO-STATS.

BY C. W. R. POWELL.

#### Errata.

In the report of the author's reply to questions, on p. 900 of the Sept. 30th, 1914, issue of this Journal, for "within half a degree" read within "one twentieth of a degree," and for "3 litres" read "3 gallons."

### Obituary.

#### HUGO MÜLLER.

Dr. Hugo Müller died suddenly, in his eighty-second year, at Camberley, Surrey, on May 23rd. He studied chemistry under Erdmann in Leipzig and Wöhler in Göttingen, where in 1853 he took the Ph.D. degree. He then went to Munich to act as assistant to Liebig, but soon came to England, on Hofmann's invitation, to assist Warren de la Rue in the investigation of Barmese naphtha; through the advice which he was able to give when consulted by Thos. De la Rue and Co. (in whose factory they had their laboratory) it became so obvious, after a time, that the services of a chemist would be of value, that he was induced to enter the firm, though originally he had intended to adopt a scientific career; he ultimately became a partner and a director when the business was made into a limited company. A man of wide knowledge, possessed of great technical skill and manipulative power, he contributed very largely to the development of the business, especially in the Stamp and Bank Note Departments in which his artistic as well as his scientific gifts were of peculiar value; he was one of the first to develop electrotyping and much improved lithographic and colour printing in this connexion; he was also a great authority on paper and the author of an important monograph on cellulose, the first to deal with the subject in any thorough manner. He retired in 1902 and then took up work in the Davy-Faraday Laboratory founded by Dr. Mond in connexion with the Royal Institution. During the past twelve years, he has been a constant attendant there, working long hours daily—not the short time which Professor Perkin recently deprecated, in his Presidential address, as customary among young students in the Oxford laboratory. Two investigations of superlative interest were carried out by him during this period—one relating to a substance (*Coccolite*) which he first met with in palm leaves but subsequently identified with the scyllitol separated from the dog-fish, an isomeride of inositol; the other to the peculiar bloom on the leaf and flower-stalk of many species of primula, which he identified with Flavone; this was previously unknown as a natural product, and the discovery is of special interest, as Flavone is the parent of a great group of yellow colouring matters present in plants. In execution, these two inquiries are models of method and remarkable as examples of the great technical skill of the school to which Dr. Müller belonged, which now unfortunately has so few followers.

Dr. Müller, at first an ardent mineralogist, through his love of Nature, gradually passed over to botany and to horticulture; during the past 30 years, he has been noted as a gardener, particularly for his knowledge of the habits of plants. He was a man who was greatly beloved by his circle of friends. He was elected a Fellow of the Royal Society in 1866. He entered the Chemical Society in 1859 and served it as Foreign Secretary from 1869 to 1885, when he became President. He was an original member of this Society.



## Journal and Patent Literature.

PATENT SPECIFICATIONS may be obtained by post by remitting as follows:—

*English*.—6d. each, to the Comptroller of the Patent Office, Southampton Buildings, Chancery Lane, London, W.C.

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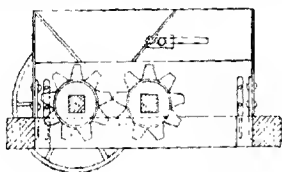
*French*.—1 fr. 05 c. each, as follows: Patents dated 1902 to 1907 inclusive, Belin et Cie., 56, Rue Feron 8, Paris (6c). Patents from 1908 to date, L'Imprimerie Nationale, 37, Rue Vieille du Temple, Paris.

### I.—GENERAL PLANT; MACHINERY.

#### PATENTS.

*Crushing apparatus*. J. Russell, London. Eng. Pat. 29,175 of 1913. Date of appl. May 7, 1914.

THE cogs of the crushing apparatus have square



teeth which work point to point, as shown.

—W. H. C.

*Crushers*. A. W. Warsen, New York. Eng. Pat. 13,337. May 30, 1914.

To prevent damage to the machinery, the oscillating lever, which carries one of the jaws, is provided with an arm mounted resiliently on the lever, so that the latter remains immovable when an object of high resistance enters between the jaws.—W. H. C.

*Filtering apparatus*. W. E. Trent, Reno, Nev., U.S.A. Eng. Pat. 16,250, April 25, 1911.

FILTER trays are mounted round the periphery of a frame, which is rotated about a horizontal axis, so that they are free to oscillate. Each tray has a suitable filter medium and a perforated pipe for the supply of washing and flushing water; the space beneath the filter medium is connected by pipes to a vacuum pump. The trays are normally maintained in a horizontal position, and are filled in succession; the liquid portion is drained away, and the cake washed if necessary. The cake is then discharged by tilting each tray as it approaches the lowest position, and flushing water is supplied, if necessary, to detach the cake.—W. H. C.

*Filter*. M. Cole, Washington, D.C. U.S. Pat. 1,137,581, April 27, 1915. Date of appl. Sept. 5, 1914.

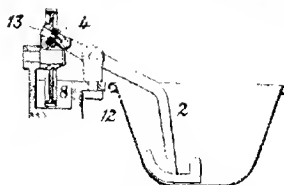
THE filter system comprises a vertical primary, a horizontal secondary, and a vertical final chamber, the final chamber being higher than the others. Each chamber is divided by a perforated partition into two compartments, of which only one contains filtering medium. The chambers are connected by piping, and a heating medium may be introduced for sterilising them.—W. H. C.

*Mixing apparatus*. R. B. Grey, London. Eng. Pat. 1890, Feb. 5, 1915.

A PROPELLER agitator, mounted and rotated on a central vertical shaft within the mixing tank, is raised and lowered by means of a cord and pulley driven from the shaft. A diverter blade is mounted in the tank near the centre of the upper part of the liquid to disturb the surface tension of the vortex caused by the propeller.—W. H. C.

*Mixing and kneading machine*. R. Herbst, Halle, Germany. U.S. Pat. 1,138,651, May 11, 1915. Date of appl. July 2, 1913.

THE kneading member, 2, pivoted in the rotating support, 12, is reciprocated by rotation of the



driving wheel, 8, through the medium of the inclined pin, 13, and ball bearing, 4.—W. E. F.

*Dryer; Centrifugal*.—C. A. Wendell, Joliet, Ill. U.S. Pat. 1,139,988, April 27, 1915. Date of appl. July 14, 1913.

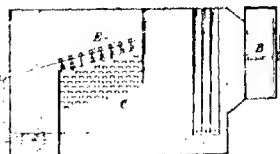
THE material to be dried is delivered into the basket from a spout, which is rotated about the same axis, and in the same direction as the basket, but at a different speed. The dried material is discharged by the centrifugal force through a trap in the bottom of the basket, which is opened at intervals.—W. H. C.

*Desiccating apparatus*. J. C. MacLachlan, Chicago, Ill. U.S. Pat. 1,138,769, May 11, 1915. Date of appl. March 16, 1911.

THE material is carried by a current of air into the upper part of a rectangular chamber at one end, and the solid particles are separated by inclined screens, which extend from the upper part of the sides to the centre line of the floor. The air passes through the screens and is discharged through exhaust ports in the side walls, near the opposite end. The separated material is removed from the chamber by a screw conveyor.—W. H. C.

*Air washing and conditioning apparatus*. W. H. Carrier, Assignor to Buffalo Forge Co., Buffalo, N.Y. U.S. Pat. 1,138,081, May 4, 1915. Date of appl. Jan. 21, 1910.

THE air or gas is drawn by the fan, B, downwards between the baffles, C, upon which the washing or



moistening liquid is sprayed from the nozzles, E.—W. H. C.

*Washing, cleaning, and cooling gases; Apparatus for*.—H. E. Theisen, Munich, Germany. U.S. Pat. 1,139,385, May 11, 1915. Date of appl. Oct. 20, 1913.

THE apparatus is divided by a partition into a

central fan compartment and lateral washing compartments. The latter are provided with several concentric, annular disintegrator members, supported on and rotated by a disc, and a suitable washing fluid is directed against the disintegrators through perforations in the disc. Means are provided for preventing liquid passing from the washing to the fan compartment.—W. H. C.

*Boiler for utilising waste heat [from regenerative metallurgical furnaces].* C. J. Bacon, Chicago, Ill. U.S. Pat. 1,138,346, May 4, 1915. Date of appl., Jan. 7, 1915.

HOT waste gases are passed successively through two communicating fire-tube boilers, placed in series, and water is fed into the cooler lower part of the second boiler.—W. H. C.

*Corrosive fumes in gases; Apparatus for neutralizing* — T. E. Murray and E. B. Ricketts, New York. U.S. Pat. 1,139,053, May 11, 1915. Date of appl., Feb. 1, 1915.

THE current of gas is caused to impinge successively upon the surfaces of a number of vertical, perforated plates, contained in a casing. A film of suitable liquid trickles over the surfaces of the plates. The liquid absorbs the impurities and flows down to the bottom of the casing, from which it is continuously elevated to a reservoir in the upper part of the casing, and flows over the plates again.—W. H. C.

*Kiln.* S. P. Beebout, New Cumberland, W. Va., and T. E. Morgan, Columbus, Ohio. U.S. Pat. 1,139,327, May 11, 1915. Date of appl., May 1, 1914.

FURNACES are arranged at intervals around the annular wall of the kiln, and the fire-gases pass through openings in the wall into "bags," or chimneys which communicate at their upper ends with the interior of the kiln. The ware is supported on a grid floor above an annular flue encircling the kiln at the inner surface of the enclosing wall, this grid floor being spaced away from a lower floor, which is not perforated except for a central opening communicating with a chamber below. The central chamber is connected by radial flues with the annular flue and by a main flue with the stack; the radial flues slope downwards towards the central chamber, and the main flue is provided with a damper for controlling the draught. The top of the annular flue is perforated between the "bags," and the inner wall of the flue has openings communicating with the space between the two floors of the kiln, the size of the openings being greater the more distant they are from the "bags."—A. S.

*Samples of liquids contained in receptacles; Apparatus for taking* — J. Acker, E. Schmitz, and L. Gourwitsch, Ger. Pat. 282,172, Feb. 19, 1914.

THE sample is collected in a hollow cylinder fitted with a piston, means being provided for lowering and raising the cylinder and, during the latter operation, simultaneously raising the piston within the cylinder. The mechanism is so arranged that the upward movements of the piston within the cylinder and of the cylinder within the receptacle are proportional to one another.—A. S.

*Filters; Pressure* — E. J. Sweetland, Montclair, N.J., U.S.A. Eng. Pat. 9019, April 9, 1914. Date of appl., April 12, 1913.

SEE U.S. Pat. 1,083,305 of 1911; this J., 1914, 341.

*Tube-mill.* W. B. Easton, Chicago, Ill. U.S. Pat. 1,139,651, May 18, 1915. Date of appl., June 8, 1914.

SEE Eng. Pat. 14,231 of 1914; this J., 1915, 89.

## IIa.—FUEL; GAS; MINERAL OILS AND WAXES.

*Coal and coke production in Germany.* Board of Trade J., May 27, 1915.

THE "Frankfurter Zeitung" of May 1st gives the following statistics of the production of coal, coke, etc., in Germany:—

	1913	1914
	Metric tons.	Metric tons.
Coal .....	191,541,151	161,545,224
Lignite .....	87,116,313	82,946,906
Coke .....	32,167,716	27,324,712
Briquettes .....	27,241,555	27,397,529

*Mineral oils; Optical activity of* — C. Engler and W. Steinkopf, Ber., 1911, 47, 3358. J. Chem. Soc., 1915, 108, i, 205-206.

SPORADIC optical activity in mineral oils can be attributed to contact with optically active animal or vegetable matter, but universal activity is a strong argument in favour of an organic origin. In examining oils for optical activity they should be separated into as large a number of fractions as possible, and these frequently require to be redistilled; otherwise optically active constituents disseminated through the mass of the oil may escape detection, particularly if both dextro- and levo-rotatory constituents are present. Mineral oils readily lose their activity, wholly or in part, when exposed to a high temperature; distillation should be effected, therefore, under the lowest possible pressure and from small vessels, superheating being avoided. The authors have found some portions with distinct optical activity in every mineral oil which they have investigated.

*Electrical excitability and conductivity of liquid insulators [benzene, light petroleum, etc.].* D. Holde, Ber., 1911, 18, 3239-3257. J. Chem. Soc., 1915, 108, ii, 209-210.

IT is well known in laundry works that when woollen goods are moved about in benzene the former become positively and the latter negatively charged, and that, on approach of the hand, a spark discharge may occur, causing ignition of the liquid. To obviate this danger, Richter has proposed the addition of magnesium oleate, the action of which probably depends on an increase in the specific conductivity of the benzene. Liquid insulators, such as ether, light petroleum, and benzene, can acquire a charge amounting to several thousand volts when pumped through metal tubes, and to minimise the danger of fire in such cases Richter has proposed that the tubes, reservoirs, etc., should be earthed. These measures have been criticised by Dolezalek (this J., 1911, 1117), who considers that in the case of good insulators the charge cannot be dissipated sufficiently rapidly in this manner. The author's experiments show that the specific conductivity of different specimens of laboratory benzene and light petroleum is  $10^{-11}$  to  $10^{-15}$ . The degree of electrical excitement of a liquid of low electrical conductivity caused by passage under pressure through narrow metal tubes depends, other things being equal, on the conductivity of the liquid, which is influenced by temperature, and moisture and other impurities. The electrical charges acquired by liquid insulators (benzene or light petroleum) by passage through narrow tubes are instantly dissipated under the conditions of the experiments by earthing the receivers when the conductivity is not less than  $10^{-15}$ . This effect does not appear to depend on the electrical conductivity of the liquid, but rather on the mechanical movement

experienced by the mobile benzene when forced into the receivers, and also on the convection currents, whereby all the charged particles are speedily brought into contact with the walls of the vessel. It is recommended that the discharge pipe should be brought close to the bottom or to the sides of the tank. The electrical excitability of liquid insulators can be diminished by addition not only of soap, but also of alcohol or acetic acid, which likewise increase the conductivity. (See also following abstract.)

*Electrical conductivity of heavy hydrocarbon oils; Influence of soaps of naphthenic acids and of phenols on the —.* D. Holde. Ber., 1915, 48, 11-19, 288. J. Chem. Soc., 1915, 108, ii, 136. (See preceding abstract.)

The electrical conductivity of heavy petroleum hydrocarbons is raised considerably by addition of calcium soaps of naphthenic acids, whereas a corresponding amount of the free naphthenic acids produces only a slight effect. The conductivity of heavy tar oils is increased in a similar manner by the presence of phenols. Heavy tar oil free from phenols has a higher conductive power than heavy mineral oil.

#### PATENTS.

*Fuel briquette.* C. J. Schneider, New York. U.S. Pat. 1,138,916, May 4, 1915. Date of appl. Dec. 9, 1914.

A mixture of molasses 15 galls., soap 15 lb., coal 1 ton, and alum 25 lb., is moulded into briquettes which are dried and then passed successively through a solution of soap and a solution of alum.—W. E. F. P.

*Coke-producing plant.* F. Tschudy, Birmingham, Ala. U.S. Pat. 1,139,688, May 11, 1915. Date of appl. June 17, 1911.

Is a by-product coke-producing plant comprising a number of regenerative reversible coke ovens, a single motor actuates the gas, air, and stack valves at both ends of each oven, so that the supply of gas to one side of each oven is discontinued simultaneously with the reversal of the air flow through it. A supply of gas is subsequently admitted from the opposite side of each oven.—W. E. F. P.

*Vertical [gas] retorts.* Drakes, Ltd., and W. A. Drake, Halifax. Eng. Pat. 8740, April 7, 1911.

The combustion-chambers surrounding the retorts are provided with regenerative flues formed by pipes built into the walls, and with means for admitting heated air at various levels.—W. E. F. P.

*Gas retorts; Vertical.*—H. J. Tonggood, and R. Dempster and Sons, Ltd., Elland, Yorks. Eng. Pat. 11,178, May 6, 1911.

To support the coal charge in the carbonising zone, a table is carried by supports pivoted on the hinged bottom lid, so that on opening the lid it falls down upon a catch in such a position as to be clear of the retort mouth on the opposite side to the lid. The coke falls out between the supports of the table.—W. E. F. P.

*Vertical [gas] retorts; Means for charging.*—J. B. Tansig, Assignor to United Gas Improvement Co., Philadelphia, Pa. U.S. Pat. 1,110,310, May 18, 1915. Date of appl. Jan. 20, 1913.

A row of coal-hoppers, arranged upon a movable carriage and provided with devices for varying the volume of, and weighing, the contents of each, is disposed above a row of retorts with which connection is made by means of shoot-funnels; the latter fit the mouths of the retorts closely and have smaller discharge openings than the hoppers,

so that the funnels are sealed by the charge during operation.—W. E. F. P.

*Gas; Method of manufacturing.*—H. A. Carpenter, Sewickley, Pa., and D. D. Barnum, Worcester, Mass., Assignors to Ritter-Conley Manufacturing Co., Pittsburgh, Pa. U.S. Pat. 1,140,113, May 18, 1915. Date of appl. July 21, 1913.

The apparatus consists of several units, each comprising two vertical series of horizontal retorts separated by a vertical stand-pipe with which each retort is connected. The vertical pipes discharge into a common horizontal main at the base of the apparatus, and the charging of the retorts is timed so that the gaseous stream in each vertical pipe is maintained practically uniform in temperature, volume, and composition.—W. E. F. P.

*Gas producers, blast furnaces, or the like.* T. Bairdow, Swansea. Eng. Pat. 18,381, Aug. 7, 1914.

In gas producers, etc., of the pressure type, each of the access openings, through which the fire is stirred and the clinker broken, is provided with a circular steam-pipe having a number of horizontal slits, so that when the plug is removed and the steam turned on, the opening is sealed by divergent jets of steam having a fish-tail form and a downward direction. The circular pipe is protected by a recessed cover disposed around the access opening.—W. E. F. P.

*Acetylene gas; Storing mass for.*—G. Dulén, Stockholm. U.S. Pat. 1,140,124, May 18, 1915. Date of appl. June 17, 1912.

A porous mass consisting of charcoal, silicious earth, fibres of elastic material, and hydraulic cement not containing free oxides, is used for storing a solution of acetylene in acetone.—W. E. F. P.

*Gas-scrubber.* W. M. Derby, Buchanan, N.Y. U.S. Pat. 1,138,460, May 4, 1915. Date of appl. Sept. 25, 1913.

Gas passes down through a vertical cylinder which contains a sprayer, and then up through the annular space between the inner cylinder and an outer concentric one. A spiral guide is arranged in the annular space, and the wall of the outer cylinder is provided with openings for the discharge of impurities, water, etc. The whole is contained in a casing.—W. E. F. P.

*Gas; Purification of.*—H. F. Smith, Lexington, Ohio. U.S. Pat. 1,110,198, May 18, 1915. Date of appl. Oct. 12, 1912.

The gas is passed through a pervious medium, whereby the particles of tar are caused to coalesce; the coalesced particles are then removed from the pervious medium by the flowing gas and separated from the latter by gravity or inertia.—W. E. F. P.

*Coke-oven gases and waste liquors containing salts of heavy metals; Purification of.*—Hochofenwerk Lübeck A.-G. Ger. Pat. 280,819, Sept. 27, 1912.

Coke-oven gas is led into the waste liquor, whereby hydrogen sulphide is removed from the gas and the dissolved salts of heavy metals are converted into insoluble sulphides. In the case of solutions containing both copper and zinc salts, the copper is first precipitated as sulphide in acid solution, and then, after neutralising the acid, the zinc is precipitated.—A. S.

*Tar separator.* Berlin-Anhaltische Maschinenbau-A.-G. Ger. Pat. 282,279, Sept. 6, 1913.

The separator comprises a hood sealed below in the liquor and consisting of an inner and an outer

casing, the latter being connected to the cover of the hog and to the inner casing by means of press-clamps or the like, so that it can be easily and rapidly removed.—A. S.

*Carbon monoxide; Removal of— from gaseous mixtures.* Badische Anilin und Soda Fabrik. Ger. Pat. 282,505, Nov. 19, 1913.

CARBON monoxide is removed by absorption, preferably under pressure, in a solution of cuprous chloride containing more than 60 grms. of ammonia, in the form of free base or carbonate, per litre. Absorption is very rapid, and the solution does not attack parts of the apparatus made of iron.—A. S.

*Mineral oils and residues; Treatment of— for the production of lower boiling hydrocarbons.* C. White, London. Eng. Pat. 5134, Mar. 3, 1914.

The oil or residue, with or without preliminary distillation, is distributed in a liquid state, and without the addition of steam, on to the surface of quicklime which has been heated to 500° to 600° C. in a retort or chamber. The vapours of lower boiling point thus produced may be drawn off by suction and fractionated. Crude paraffin oil thus treated yields 20 to 25% of hydrocarbons with flash-point and boiling point similar to those of petrol.—C. A. M.

*Hydrocarbon oils; Process of treating—.* C. H. Washburn, Assignor to New Process Oil Co., St. Louis, Mo. U.S. Pat. 1,138,266, May 4, 1915. Date of appl., Mar. 24, 1913.

KEROSENE and petroleum products of 26° to 48° B. (sp. gr. 0.901–0.791) are transformed into a product of Baumé not exceeding 52 (sp. gr. 0.777) by heating with water in a retort at 650° to 950° F. (340°–510° C.), and condensing the vapours under a pressure of 3 to 5 atmos. which is maintained both within the retort and the condenser.—C. A. M.

*Coal-gas-retort chambers and the like; Heating—.* J. M. Rusby, Assignor to The United Gas Improvement Co., Philadelphia, Pa. U.S. Pat. 1,140,337, May 18, 1915. Date of appl., June 27, 1914.

SEE Eng. Pat. 22,425 of 1914; this J., 1915, 413.

*Gaseous mixture; Combustible—.* F. P. Peterson, Tulsa, Okla., U.S.A. Eng. Pat. 12,006, May 15, 1911. Under int. Conv., Jan. 5, 1911.

SEE U.S. Pat. 1,094,861 of 1914; this J., 1914, 855.

## II.—DESTRUCTIVE DISTILLATION; HEATING; LIGHTING.

*Hardwoods; Yields from the destructive distillation of certain—.* L. F. Hawley and R. C. Palmer. Bull. U.S. Dept. Agric., No. 129, Sept. 10, 1911, 16 pages. (See also this J., 1911, 315).

The gas-retort used in the tests had an oil-jacket and pyrometer tubes, and except that it was relatively small and the maximum temperatures obtained were low, the conditions of distillation were the same as in commercial practice. When arranged according to yield of wood alcohol the order was beech, maple, birch, beech being the best; for acetic acid the order was birch, beech, maple. The absolute yields were different for woods from different localities, but the relative order was the same. Chestnut gave the lowest yield of alcohol but was among the highest for acid; with hickory the alcohol yield was very high, the acid yield very low. The presence of bark reduced the yield of both acid and alcohol, but

maple bark gave very nearly as much alcohol as the wood itself. For yield of tar the order was: hickory, maple, birch, beech, oak, chestnut; for charcoal: chestnut, oak, beech, maple, birch, hickory. These results are calculated on the basis of percentage dry weight of wood distilled; on the commercial basis of yields per cord (90 cub. ft.) of wood, the positions of hickory and oak would be improved, and those of chestnut and the lighter woods correspondingly lowered.—E. H. T.

*Emissivity of metals and oxides. II. Measurements with the micropyrometer.* Burgess and Waltenberg. See XXIV.

## PATENTS.

*Distillation of coal or the like; Destructive— with addition of steam.* A. Heckert. Ger. Pat. 282,355, March 6, 1914.

A HORIZONTAL retort is divided into three compartments by vertical partitions. Steam is introduced into the rear compartment, which is provided with baffles of refractory material. After being thus superheated, the steam passes through an opening at the bottom of the dividing wall into the next compartment, which is filled with graphite. In passing through this compartment the steam is decomposed, and the decomposition products pass through an opening at the top of the dividing wall into the third compartment, which is larger than the others and serves as carbonising chamber for the coal or the like.—A. S.

*Surface combustion burner.* E. J. Allen, Assignor to Rathbone, Sard, and Co., Albany, N.Y. U.S. Pat. 1,139,321, May 11, 1915. Date of appl., Feb. 10, 1915.

THE gas mixture passes from a mixing chamber through openings in a superposed firebrick hearth, and is burnt against inclined baffle plates mounted on the hearth. The entire surface of the hearth is thus rendered incandescent and yields heat by radiation to the object to be heated.—W. F. F.

*Electrodes; Preparing arc-lamp—.* G. M. Little, Pittsburgh, and B. J. Gudge, Wilkinsburg, Pa., Assignors to Westinghouse Electric and Manufacturing Co. U.S. Pat. 1,138,674, May 11, 1915. Date of appl., April 24, 1910.

ROD-LIKE electrodes, containing a volatile binder, are baked by moving them into and out of a furnace, and simultaneously rotating them axially. A current of air is directed upon them to remove liberated carbonaceous gases.—B. N.

## III.—TAR AND TAR PRODUCTS.

*Isoquinoline in coal tar.* R. Weissgerber. Ber., 1914, 47, 3175–3181. J. Chem. Soc., 1915, 108, i., 302–303.

ISOQUINOLINE occurs to the extent of less than 1% in the crude quinoline obtained from coal tar, and was isolated from this source by Hoogwerff and van Dorp by fractional crystallisation of the hydrogen sulphates. A process has now been devised for its extraction on the large scale. Isoquinoline is more basic than quinoline, and by shaking a benzene solution of the crude oil with enough 20% sulphuric acid to combine with about one-sixth of the base, the extract is considerably enriched in isoquinoline. The enriched base, recovered from the acid solution, is fractionated, and the quinoline fraction is separated by the old method. Apparently, the two quinolines are the only tar bases the sulphates of which are precipitated in alcoholic solution, so that the original

crude tar-oil bases may be treated in this way with advantage, without first isolating the crude quinoline. *α*-Isoquinolinesulphonic acid is easily isolated by adding the crude sulphates (above) to cold sulphuric acid containing 50% of the anhydride. It seems impossible to convert this into isoquinoline, however. When it is fused with potassium hydroxide, *α*-hydroxyisoquinoline is produced at 200–250° C., but a dihydroxyisoquinoline is formed if the fusion is carried out at 300° C. This compound is no longer basic, but dissolves in sodium carbonate and gives orange-red azo dyes. It forms pale yellow needles from water, m. pt. 273° C. (decomp.).

*Sulphonic acids: Conversion of aromatic — into phenols.* F. Willson and K. H. Meyer. Ber., 1911, 47, 3160–3163. Bull. Soc. Chim., 1915, 18, 144.

WILSON dilute alkali hydroxides only partially transform benzenesulphonic acid into phenol above 300° C., good yields of the pure naphthols are obtained from *α*- and *β*-naphthalenesulphonic acids by treatment with 10% sodium hydroxide at 300° C. Benzenedisulphonic acid gives under similar conditions *m*-phenolsulphonic acid, whilst *o*- and *p*-phenolsulphonic acids yield phenol, and also, in the former case, traces of catechol. From both chlorobenzenesulphonic acid and dichlorobenzenesulphonic acid one halogen atom is eliminated, the sulpho group being unattacked, and phenolsulphonic acid and chlorophenolsulphonic acid respectively being formed. The alkaline earths and sodium carbonate act very feebly on the sulphonic group. —G. F. M.

*Alkylated p-phenylenediamines and derivatives. Quinonimide-ammonium compounds.* R. Meldola and W. F. Holly. Chem. Soc. Trans., 1915, 107, 810–822.

ACETYLATED UN-SYMMETRICAL dialkylated *p*-phenylenediamines of the type  $C_2H_5O.NH.C_6H_4.N.A.b$  were prepared from alkylated anilines by converting these into their nitroso derivatives and subsequently reducing and acetylating. Methylacetyl-*p*-phenylenediamine, silky needles, m. pt. 92° C., readily combines with alkyl iodides to form crystalline quaternary ammonium iodides; the free quaternary bases are syrupy liquids, which rapidly absorb carbon dioxide from the atmosphere. The propyl and allyl compounds containing an asymmetric nitrogen atom form non-crystallisable syrups with optically active acids. Dimethylacetyl-*p*-phenylenediamine, m. pt. 132–133° C., and benzylmethylacetyl-*p*-phenylenediamine, m. pt. 110–111° C., were prepared from dimethylaniline and benzylmethyl-*p*-nitroaniline respectively. Only the dimethyl compound gave quaternary ammonium compounds, and its methiodide was converted through the nitrate into a quinonimide-ammonium compound by the action of nitric acid. This compound, to which the structure  $NH:C_6H_4(NO_2)_2:N(CH_3)_2$  is assigned, forms golden scales, m. pt. 200–220° C. (with decomp.). It gives a colourless dihydrochloride. All the above-mentioned dialkylacetylphenylenediamines are converted on nitration into 3,5-dinitro-1-acetylaminophenyl-1-methylnitrosamine,  $C_6H_4O.NH.C_6H_4(NO_2)_2.N(CH_3)_2NO$ , m. pt. 152–153° C., which on boiling with phenol is transformed into dinitromethylacetyl-*p*-phenylenediamine, scarlet needles m. pt. 196–197° C. The de-acetylated diamine forms purple needles, m. pt. 186° C. —G. F. M.

*Electrical excitability and conductivity of liquid insulators (benzene, light petroleum, etc.). Influence of soaps of naphthenic acids and of phenols on the electrical conductivity of heavy hydrocarbon oils.* Holde. See II A.

#### PATENTS.

*Aromatic amines: Preparation of —.* Farb. vorm. Meister, Lucius, und Brüning. Ger. Pat. 282,492, Oct. 2, 1913.

NITRO-COMPOUNDS are volatilised with steam and the mixture is passed together with hydrogen over catalysts heated to a temperature considerably below the boiling-point of the nitro-compound. For example, nitrobenzene is heated to 120° C. and a mixture of steam and hydrogen passed through the liquid; the mixture is passed through a long tube half-filled with finely divided nickel, and the vapours are condensed. The yield of aniline is almost theoretical. —F. W. A.

*Aromatic carboxylic acids chlorinated in the nucleus: Preparation of —.* Farb. vorm. Meister, Lucius, und Brüning. Ger. Pat. 282,133, July 10, 1913.

AN aromatic sulphonic acid or one of its salts, containing methyl groups in the ring, is heated above 200° C. with thionyl chloride, with or without an indifferent solvent. According to the temperature mono-, di-, or tri-chloro derivatives are obtained, which form acids on heating with warm water, alkalis, or acids; for example, *o*- or *p*-toluenesulphonic acid gives an excellent yield of *o*- or *p*-chlorobenzoic acid in a high state of purity. —F. W. A.

*2,5-Diaminodiarlylmonosulphones and 2-amino-5-mono- or di-alkylaminodiarlylmonosulphones: Preparation of —.* Anilinfarben-u. Extrakt.-Fabr. vorm. J. R. Geigy. Ger. Pat. 282,211, Aug. 3, 1913.

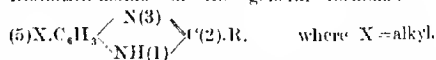
ONE mol. of an aromatic *p*-diamine or of its asymmetric *N*-mono- or di-alkyl derivatives is oxidised with 1 mol. of an aromatic sulphonic acid; the products may be diazotised for use in the preparation of azo-dyestuffs. —F. W. A.

*Unsaturated acids of the anthraquinone series: Preparation of —.* Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 282,265, Dec. 7, 1913.

ANTHRAQUINONE-2-ALDEHYDE, *ω*-dihalogen-2-methylanthraquinone, or a derivative of either, is condensed with an acetate. In this manner anthraquinonyl-2-acrylic acid has been prepared for the first time. —F. W. A.

*Amino-derivatives of substituted benzimidazoles: Preparation of —.* D. Maron. Ger. Pat. 282,374, Feb. 25, 1913.

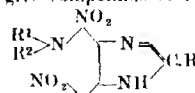
BENZIMIDAZOLES of the general formula:



halogen, or oxyalkyl, and *R* = hydrogen, alkyl, OH, or  $NH_2$ , are treated with concentrated sulphuric acid and nitrates. The 4,6-dinitro-compounds obtained are entirely or partly reduced to diamines or nitroamines, which are important intermediate products for the preparation of dyestuffs. —F. W. A.

*Basic condensation products of the benzimidazole series: Preparation of —.* D. Maron. Ger. Pat. 282,375, Aug. 14, 1913.

THE 4,6-dinitro-5-halogen-benzimidazoles, obtained as described in the preceding abstract, are condensed with primary or secondary aliphatic amines or primary aromatic amines or their substitution products to give compounds of the type:



where *R* = hydrogen, alkyl, OH, or  $NH_2$ ;  $R^1$  = alkyl,  $C_6H_5$ ,  $C_6H_4OH$ ,  $C_6H_4COOH$ ,  $C_6H_4NH_2$ .

( $C_6H_5S_2$ ,  $C_6H_5SO_3H$ ; and  $R^2$ =hydrogen, or alkyl when  $R^1$  also is alkyl. The products may be used in the preparation of dyestuffs and pharmaceutical products.—F. W. A.

*N-Antraquinonylsatins: Preparation of* —. Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 282,490, Feb. 27, 1914.

Acid chlorides, such as benzoyl chloride, acetyl chloride, chlorocarbonic acid ester, phosgene, etc., have no action on *N*-monoarylaminoanthraquinones, but oxalyl chloride gives characteristic products on addition of condensing agents such as aluminium chloride, ferric chloride, or phosphorus pentoxide. The products are *N*-anthraquinonylsatins, which are valuable in the preparation of dyestuffs.

—F. W. A.

*Hydrogenation [reduction of aromatic nitro-compounds]: Process of* —. A. Brochet, Paris. Eng. Pat. 22,523, Oct. 6, 1913. Under Int. Conv., Oct. 8, 1912. Addition to Eng. Pat. 16,936 of 1913, dated July 27, 1912.

See Addition of Oct. 8, 1912 to Fr. Pat. 458,033 of 1912; this J., 1914, 18.

#### IV.—COLOURING MATTERS AND DYES.

*Indigo: The "wilt" disease of Java* —. Rept. on the Progress of Agriculture in India for 1913-14.

The disease known as "wilt," to which Java indigo is subject, and which has caused a reduction by nearly 80% in three years in the area under this variety in Bihar, has been investigated at Pusa and found to be due to a continued wet condition of the soil. By sowing Java indigo for seed early in August on well-drained land, the disease has been avoided.

*Indigo in China: Production of natural* —. Board of Trade J., May 27, 1915.

The United States Consul-General in Hongkong states that the shortage of the supply of synthetic indigo has led to a revival of the production of indigo in various parts of China. Indigo production is one of China's oldest industries. It is unlikely, however, that there will be any of the product available for export, for the time being at least.

*Diazo-oxides (diao-phenols): Constitution of internal* —. G. T. Morgan and J. W. Porter. Chem. Soc. Trans., 1915, 107, 645-659.

From a survey of existing evidence it is concluded that the internal diazo-oxides probably possess the cyclic diazo-oxide structure,  $C_6H_4 \begin{smallmatrix} O \\ \diagup \diagdown \\ N \end{smallmatrix}$ . The

non-formation of internal *meta*-diazo-oxides from *m*-hydroxydiazonium salts, whilst *ortho*-, *para*-, and *peri*-diazo-oxides are readily produced, excludes the diazonium structure, which represents them as internal salts; such salts should be formed by *meta*-compounds with equal facility. The influence of a nitro group on the diazo-oxide formation was studied in the nitroaminophenols. 2-Nitro-1-aminophenol and 5-nitro-2-aminophenol yielded on diazotisation their respective diazo-oxides even in acid solution, whilst diazotised 3-nitro-1-aminophenol gave no oxide even on neutralising with sodium bicarbonate, but the product was obtained by treating the aminophenol with nitrous fumes in ethereal solution. The above diazo-oxides form yellow or red crystals which explode violently when heated. They combine readily with  $\beta$ -naphthol or resorcinol giving red azo derivatives. The sparingly soluble metallic

salts of 4-nitro-2-hydroxybenzeneazo- $\beta$ -naphthol, prepared by adding an aqueous solution of the metallic salt to an alcoholic solution of the azo compound and neutralising with ammonia, are intensely coloured lakes; the alkali salts are blue; magnesium, crimson; zinc, blue; calcium, purple; lead, bluish green; chromic, bluish grey; nickel, purple, and cobalt, dark green.—G. F. M.

*Arylamides of m-nitrobenzenesulphonic acid: Molecular rearrangements among* —. O. N. Witt and H. Truttwin. Ber., 1914, 47, 2786-2795. Chem. Zeit., 1915, 39, Rep., 126.

*p*-TOLYLNITROBENZENESULPHAMIDE was prepared from *m*-nitrobenzenesulphor chloride and *p*-toluidine. Subsequent treatment with dimethyl sulphate gave the methyl derivative, which in presence of concentrated sulphuric acid changed to the intensely coloured nitro-sulphone. This was acetylated with acetic anhydride and sulphuric acid and reduced to the corresponding amine by means of stannous chloride and hydrochloric acid. An orange-red azo-colour was produced by diazotising the amine and combining with *R*-salt. Alkaline reducing agents converted the above nitro-sulphone,  $(3)NO_2.C_6H_4.(1)SO_2.(6)C_6H_4(CH_3).NH.CH_3(1,1)$ , into the intensely yellow azoxy-compound, which was readily reduced further with stannous chloride and hydrochloric acid. The resulting base was isolated from the almost insoluble tin double salt; upon diazotising and combining with *R*-salt it yielded a violet dye. The uncombined tetrazo-compound gave a dimethyl-di-*p*-tolylidiphenyldisulphone when heated with ethyl alcohol and copper sulphate.—J. R.

*Orazine group: Synthesis in the* —. F. Kehrman and A. A. Neil. Ber., 1914, 47, 3102-3109. J. Chem. Soc., 1915, 108, i, 393-394.

3,3-NAPHTHOPHENOXAZINE was prepared by heating an intimate mixture of *o*-aminophenol and 2,3-dihydroxynaphthalene gradually to 200° C. in a current of carbon dioxide; steam was evolved at 140°-150° and the mass solidified at 160°-170° C. The powdered product was boiled with small volumes of very dilute hydrochloric acid as long as the filtrate deposited crystals, when the dried residue was crystallised from a mixture of benzene and alcohol. 3,3-Naphthophenoxazine (benzo-2,3-phenoxazine) forms colourless leaflets, m.p. 302° C., which give a magenta solution in concentrated sulphuric acid. The other product of the reaction, deposited from the filtrate is *o*-hydroxy-phenyl-3-hydroxy- $\beta$ -naphthylamine,  $HO.C_6H_4.NH.C_{10}H_6OH$ ; it crystallises in colourless needles, m.p. 155°-156° C., and is produced in greater quantity if the temperature of the reaction is moderated. When it is heated above 200° C. ring condensation takes place. The naphthophenoxazine is exposed to the air. The acetyl derivative of 3,3-naphthophenoxazine, m.p. 151° C., was nitrated by fuming nitric acid in ice-cold glacial acetic acid; a dark red, explosive tetranitro-3,3-naphthophenoxazine separated from the reaction mixture (solution in very dilute alkali hydroxide, violet; in concentrated sulphuric acid, blood-red), whilst the mother liquor deposited an orange-yellow substance on dilution. The latter was repeatedly washed with very dilute alcoholic sodium hydroxide, which dissolved polymnitro-compounds with a violet colour, and left a hydrolysed mononitro-derivative. The latter, probably 2-nitro-3,3-naphthophenoxazine, formed very long, dark brownish-red, glistening needles, m.p. 222°-223° C. (decomp.).

Catechol and *o*-aminophenol only condense to a slight extent when gently boiled together in an open vessel, but good yields of phenoxazine may be obtained by heating catechol and *o*-aminophenol with a little of the hydrochloride of the latter.

or even by heating *o*-aminophenol with its own hydrochloride at 240° C. The colourless mother liquors of many phenoxazines as obtained by the old condensations regularly developed violet colours and then deposited much more of the phenoxazine than mere evaporation would warrant. This is now explained by the presence in the mother liquors of intermediate products analogous to the above *o*-hydroxyphenyl-3-hydroxy-2-naphthylamine.

*Adsorption [of dyes, alkaloid salts, etc.] from aqueous solution:* Influence of the nature of the adsorbent in —, H. Freundlich and A. Poser. *Kolloid-Chem. Beihefte*, 1914, 6, 297—328. *J. Chem. Soc.*, 1915, 108, ii, 233—234.

COMPARATIVE experiments were made on the adsorption of basic and of acid dyes, and of salts of the alkaloids and certain other organic bases by alumina, bole, and animal charcoal.

In nearly every case the variation of the quantity of adsorbed substance with the concentration of the aqueous solution can be represented by means of the usual adsorption equation. The quantity of strychnine nitrate taken up from solution by bole and animal charcoal is, however, nearly independent of the concentration, and the adsorption equation is not applicable in this case. The assumption that a positive adsorbent will adsorb only acid dyes and a negative adsorbent only basic dyes is at variance with the results obtained. There is undoubtedly a preferential adsorption in the above sense, but basic dyes are adsorbed by positive alumina to quite an appreciable extent. The negative colloid arsenious sulphide is adsorbed by positive alumina; the positive colloid ferric hydroxide is similarly adsorbed by negative bole, and both colloids are adsorbed by neutral charcoal. In all three cases, the quantity of adsorbed colloid is independent of its concentration in the aqueous layer. Some experiments were also made with aqueous solutions of benzoic and of salicylic acid, and with solutions containing both these acids. Each acid is adsorbed from the mixed solutions in accordance with an exponential equation, and the total acid adsorbed is practically equal to that which would be adsorbed from a solution of either of the acids the concentration of which is equal to that of the mixture.

*Tides and kaolins: Adsorption capacity of — [for dyes].* P. Rohland. *Kolloid. Zeits.*, 1914, 15, 180—182. *J. Chem. Soc.*, 1915, 108, ii, 234.

THE adsorption power of tides and kaolins may be employed in differentiating between crystalline and colloid dyes, the adsorption increasing with the colloid character of the dye-stuff. Since the adsorption capacity of the kaolins, as well as the plasticity and the readiness with which they adhere to vegetable fibres, are dependent on the colloid character of the kaolin, their behaviour towards organic dyes may be employed in forming an estimate of the suitability of the kaolins for use in the ceramic and paper industries.

*Colour and constitution of the monomimics derived from phenylisomorphthiazoninium.* VI. Quinonimide dyes. F. Kehrman, R. Speidel, and E. Grandmougin. *Ber.*, 1914, 47, 3363—3369. *J. Chem. Soc.*, 1915, 108, i, 316—317.

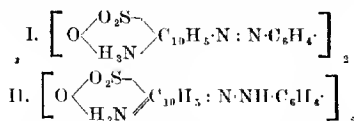
THE authors have examined the seven known isomeric monomimics derived from phenyl-*o*-naphthophenazonium, each of which forms three series of salts. The first group comprises such amines as contain the NH<sub>2</sub> group in the benzenoid nucleus of the naphthalene. The di-acidic salts are orange-yellow, resembling the mono-acidic salts of the parent substance; the tri-acidic salts are brownish-red. The mono-acidic salts and the

bases show marked differences; the former are yellowish-green in the case of the 6-amine, bluish-green (7-amine), and intensely violet (8-amine). The parent base and the 6- and 8-amines yield comparatively stable, lemon-yellow  $\lambda$ -bases when treated with an excess of alkali, whereas the 7-amine gives a blue base, probably amphiquinonoid in character, which passes into a greenish-yellow  $\lambda$ -base. Spectroscopically, the mono-acidic salts of the parent substance and the di-acidic salts of the three amines behave identically, and an ortho-quinonoid structure is indicated. The second group contains the 2- and 9-amines which contain the amino-group in the para-position to the quinquivalent nitrogen atom. The di-acidic salts are green or blue; the tri-acidic salts are brownish-purple red (9-amine) and violet-brown (2-amine). Comparison of their spectra in both the visible and invisible region with those of the di-acidic salts of the parent substance indicates an ortho-quinonoid structure. The colour changes observed during the conversion of the mono- into the di-acidic salts point to a para-quinonoid structure for these series, but spectroscopic determinations indicate an ortho-quinonoid formula. The 3-amine, which contains an amino-group in the para-position to the trivalent nitrogen atom of the azine nucleus, gives a red imino-base, soluble in ether, the shade of which is somewhat yellower than that of the violet-red mono-acidic salt, a green di-acidic salt, and a violet-brown, ortho-quinonoid tri-acidic salt. The 10-amine behaves as an ortho-quinonoid amine, giving a greenish-yellow mono-acidic, an orange-yellow di-acidic, and a violet-brown tri-acidic salt, as well as a lemon-yellow pseudo-base soluble in ether.

*Congo dyes: Blue and red — Theory of indicators.* A. Hantzsch. *Ber.*, 1915, 48, 158—167. *J. Chem. Soc.*, 1915, 108, i, 321—322.

THE usual assumption that the Congo-red salts are azo-compounds, whilst the blue acid is a quinonoid substance, is not a complete explanation of the colour change when the dye is used as an indicator, for a red acid, optically identical with the alkali salts, may actually be isolated. The existence of this red acid accounts for the peculiar behaviour of Congo Red when used as an indicator in the presence of alcohol or acetone. An aqueous solution of Congo Red is rendered blue by carbon dioxide, but an alcoholic solution is only gradually changed, through brown tones to blue, by relatively excessive addition of a mineral acid. Conversely, when alcohol or acetone is added to a solution just rendered blue by a mineral acid, the colour reverts to red. Under certain conditions the change from red to blue may be followed like a time reaction, and Congo Red is, therefore, in no sense of the word an indicator, except in pure aqueous solutions. Within certain limits, all these solutions, red salt, red acid, and blue acid, can be obtained optically empty, as revealed by the ultra-microscope. Moreover, the change into the colloidal condition is not accompanied by a distinct change of colour, but only by gradual shading, due no doubt to the stronger reflexion of the macroscopic particles. Indicator changes are, therefore, purely chemical in their origin, that is, due to isomerism. The isomeric Congo-acids are in equilibrium in solution, and this equilibrium is dependent first of all on the nature of the solvent, and only secondly on the concentration of the hydrogen or hydroxyl ions. In aqueous solutions, one chromo-isomeride is "alkali-stable," the other "acid-stable," but in presence of alcohol the equilibrium is not so quickly displaced in favour of either form. The absorption curves of the two acids are much the same in the ultra-violet, but absolutely different in the visible

spectrum. The difference in constitution of the two isomerides must therefore be fundamental, and the red acid (I.), like the salts, is most probably azoid, whilst the blue acid (II.) is quinonoid.



The blue Congo-acid may be precipitated by ether from the red solutions in alcohol or acetone. The red Congo-acid is prepared by dissolving the blue acid in pyridine and heating the red, micro-crystalline pyridine salt at 120°–130° C., when the base is expelled. There is no change in weight either in forming the red acid from the blue by this means or during the reversion to the blue acid, which is effected by a trace of hydrochloric acid. Small quantities of the red acid may be obtained more conveniently by evaporating alcoholic or acetone solutions. Two isomeric acids may also be isolated from benzopurpurin.

*Helianthins and aminoazobenzene salts: Isomerides of —.* A. Hantzsch. Ber., 1915, 48, 167–180. J. Chem. Soc., 1915, 108, i., 322–324.

ON evaporating alcoholic solutions of helianthin with about 10% of its sodium salt in platinum or silica vessels, the Methyl Orange so depresses the hydrogen-ion concentration of the helianthin that the yellow form is prevented from changing into the red. The brownish-yellow helianthin is considerably more soluble than the red modification and decomposes about 35° lower, namely, at about 200° C. Many other helianthins have been examined. With two exceptions, their red forms are stable and the yellow are either labile or unknown. The exceptions are the simplest helianthin, namely, aminazobenzene-sulphonic acid and dimethyl-*o*-toluidineazobenzene-sulphonic acid. In these cases, the stable form is yellow and the red form is labile. The red modifications are obtained by rubbing the yellow forms, but, whereas the red aniline derivative becomes yellow when merely breathed upon, the *o*-toluidine derivative has to be left in contact with water to bring this about.

A third class of chromo-isomeric helianthins consists of graphite-black products, which, like the corresponding aminoazobenzenes contain five amino-hydrogenatoms. Such are the monomethyl-, dimethyl-, monoamyl-, and monobenzyl-helianthins. They change into the red or yellow forms in the appropriate solvents.

All yellow helianthin solutions are optically similar, in alcohol or alkalis, and the absorption curves are quite distinct from those of azo-compounds. Most of the red helianthin solutions show bands like those of magenta, that is, the red forms are quinonoid. The absorption curves are, moreover, very similar to those of the yellow helianthins. These red and yellow modifications must therefore be chemically similar, and are regarded as valency isomerides.

The abnormal red modifications are those derived from dimethyl-*o*-toluidine, namely, dimethyl-*o*-toluidineazobenzene, C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>, m.p. 98° C., and the corresponding sulphonic acid: they have an azoid structure.

The common Methyl Orange itself exists in two chromo-isomeric forms. The orange salt becomes deep red on rubbing, but changes again to orange when the substance is breathed upon. They may also be valency isomerides.

It is therefore established that there are four different solid isomerides of the helianthins, three of which exist in solution, namely, an azoid form,

a black quinonoid form, and the orange-yellow and red quinonoid, valency isomerides.

*Stilbenearsinic acids and their derivatives.* Karrer. See XX.

#### PATENT.

*Colour lakes from vegetable substances containing the dyestuff as glucoside; Process for the production of —.* E. Hagen. Ger. Pat. 281,423, Nov. 19, 1912. Addition to Ger. Pat. 250,387 (see Fr. Pat. 438,563, of 1911; this J., 1912, 650).

DYESTUFF glucosides are decomposed in the usual manner by heating with acids or by enzymes, and the dyestuff is separated and converted into a lake by heating with alkaline-earth or metallic salt solutions. An alternative method is to treat the glucoside direct with an organic aluminium salt or with aluminium hydroxide, at the ordinary or a higher temperature. The lakes produced at the ordinary temperatures do not possess pronounced colouring properties. Lakes obtained by the first process are unaffected by organic acids, but this is not the case with lakes obtained by the alternative method.—F. W. A.

#### V.—FIBRES; TEXTILES; CELLULOSE; PAPER.

*Cellulose; Hysteresis of the extent of hydration of —.* Adsorption. XI. A. V. Rakovski. J. Russ. Phys. Chem. Soc., 1915, 47, 18–21. J. Chem. Soc., 1915, 108, ii., 235.

THE author has investigated, by van Bemmelen's method ("Die Adsorption," Dresden, 1910), the chemical hysteresis of cotton-wool, filter-paper, flax, and hemp at 19° C., the last two having been previously washed successively with water, alcohol, ether, alcohol, and water. The curves connecting vapour pressure with the proportion of water present are almost coincident for filter-paper and cotton-wool, but at pressures exceeding 12 mm. the former contains rather more water than the latter. For the conditions employed, the velocity of adsorption is greater than for starch, the attainment of equilibrium occupying five to seven days, or, for pressures above 14 mm., three to five days; in a desiccator containing 1% sulphuric acid solution the establishment of equilibrium is doubtful. In general, dehydration proceeds more slowly than hydration. The hysteresis exhibits a maximum of 1.8% of water, and is somewhat less than with starch. Separate calculation of the hydration and dehydration results obtained by Masson and Richards (this J., 1907, 89) for cotton-wool and filter-paper shows them to be in very fair agreement with those obtained by the author.

*Paper-making materials: The Empire's resources in —.* S. C. Phillips. J. Roy. Soc. Arts, 1915, 63, 613–632.

GREAT Britain itself does not offer much in the way of fibrous materials capable of development as new sources of supply for paper-making. Marram grass gives a fibre similar to esparto, but the yield is low. Attempts to utilise peat fibre have proved commercially unsuccessful. In Canada the total area of forest land is estimated at 500–600 million acres, about half being of commercial value. The Canadian statistics for 1914 show the manufacture of pulp from 831,538 cords of spruce, 311,183 of balsam fir, 15,246 of hemlock, 24,715 of jack pine, and 3815 of poplar, a total of 1,222,327 cords. Of this 52.6% was used for the manufacture of mechanical pulp, 33.1% for sulphite, 14% for sulphate, and 0.3% for soda pulp. Conservation and regulation of the timber



resources are receiving attention. Experiments have been made with "milkweed," which furnishes a long, fine and glossy bast fibre and a woody portion from which useful paper-pulp can be made (see Neish; this J., 1913, 72). Newfoundland forests cover over 10,000 sq. miles, with an average yield of 10 cords of pulp wood per acre; in the year ending June 30, 1913, 57,500 tons of pulp and 41,100 tons of paper were exported; the rate of increase latterly has been very rapid. In India the development of bamboo as a source of cellulose pulp has every prospect of success as soon as the limitations of the world's supply of pulp-wood produce the demand. Locally certain grasses, such as bahi or subhai, are in steady use and many other species are available. Other Indian materials capable of development are *Hedychium coronarium*, Moya grass, and cotton-seed hull fibres. In Trinidad, sugar-cane bagasse, bamboo, and Para grass have been worked on a small scale. In Australia, one mill is producing sulphate pulp from a species of pine, and proposals have been made for utilising bagasse, prickly pear, various rushes, "black-boy," eucalyptus wood, etc. New Zealand possesses a plentiful supply of suitable timber; waste from the manufacture of Phormium fibre is also available. In Africa, the papyrus and many grasses of cane-like habit are found, e.g., tamboukie grass, elephant grass, and Spanish reed (*Arundo donax*). In the Malay States,alang grass is abundant and has been approved on investigation; other fibres, such as those from pineapple and nipa palm, have been studied, with promising results.—J. F. B.

*Adsorption capacity of talcs and kaolins [for dyes].* Rohland. See IV.

#### PATENTS.

*Paper stock; Method of removing ink from —.* M. Cline and C. F. Rhodes, Glens Falls, N.Y., Assignors to International Paper Co., New York. U.S. Pat. 1,138,085, May 4, 1915. Date of appl., Nov. 27, 1911.

WASTE newspaper or book stock is pulped and about 2% of caustic soda is added to "lift" the ink. About 2% of an aluminium silicate, such as fullers' earth, kaolin, etc., or magnesium silicate, such as talc, soapstone, etc., is added to absorb the "lifted" ink, and is subsequently washed out of the stock. —W. H. C.

*Wood fibre; Process of preparing —.* J. H. Thickens, Buffalo, N.Y. U.S. Pat. 1,138,907, May 11, 1915. Date of appl., Jan. 21, 1914.

Wood is steamed under pressure in a digester until it is heated throughout; a large quantity of alkaline liquor at a temperature below the boiling point is then admitted rapidly through the bottom of the digester; the steam in the pores of the wood is thereby condensed, and the alkaline liquid drawn into the wood; the excess of liquid is then drained off and the wood is again steamed until it acquires an acid reaction. The process of alternate chilling with alkaline liquid and steaming may be repeated until the material is sufficiently digested. —J. F. B.

*Cellulose; Treatment of wood and similar fibrous materials with solutions of bisulphites, especially alkaline-earth bisulphites, for the production of —.* C. G. Schwalbe, Ger. Pat. 282,050, June 14, 1913.

The fibrous material is impregnated with the bisulphite solution, preferably *in vacuo*, the liquid is removed, and the material is steamed, with or without addition of gaseous sulphur dioxide. According to the working conditions either cellulose or half-stuff is obtained. The yield is higher than

by the boiling process, and a smaller quantity of waste lye is produced.—A. S.

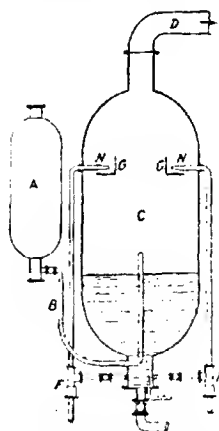
*Waste [wood-pulp] liquor; Process of recovering the soda content of —.* Method and means for treatment of waste liquor. H. K. Moore, Berlin, N.H. U.S. Pats. (A) 1,137,779, and (B) 1,137,780, May 4, 1915. Dates of appl., Mar. 6 and Aug. 11, 1913.

(A) WASTE liquor from wood-pulp is mixed with a "carbonaceous carrier" and sodium sulphate, the mixture is dried by the gases from the combustion of a previous quantity, burned in a smelting furnace, and the smelted soda recovered. (B) An intensely hot flame is produced by the incomplete combustion of fuel in the lower part of a retort, and the waste liquor from wood-pulp is sprayed with an air-blast through the flame in the upper part of the retort in order to evaporate the liquid therefrom during transit. The residue is accumulated on the sloping floor of the retort and burnt by injecting a blast of air into the upper portion of the heap; the soda is smelted in a reducing atmosphere and withdrawn from the retort in a molten state. —J. F. B.

*Waste sulphite liquor; Process of reducing — to a powder.* F. H. Kennard, Newton, Mass. U.S. Pat. 1,138,118, May 4, 1915. Date of appl., Jan. 2, 1914.

THE waste liquor is concentrated to a viscous state *in vacuo* and the product is applied in the form of a thin film to a heated surface also *in vacuo*, being retained thereon until it is dry. —J. F. B.

*Sulphite-cellulose waste lyes; Concentration of lyes, especially —.* E. Lehmann, Ger. Pat. 282,950, Dec. 12, 1912.



THE hot waste lye is discharged under pressure from the boiler, A, through the pipe, B, into the vessel, C, where a lower pressure prevails. The steam evolved escapes at D, and the residual liquor is drawn into the steam injectors, E, and discharged, together with the steam, through nozzles, N, against baffles, G. The lye is thus atomised, and a high degree of concentration is attained. —A. S.

*Retting process.* M. A. Adam, London, and W. J. Fernie, Dromara, Ireland. U.S. Pat. 1,140,296, May 18, 1915. Date of appl., Jan. 9, 1905.

SEE Eng. Pat. 715 of 1914; this J., 1915, 515.

*[Paper] pulp, stuff, and the like; Apparatus for refining —.* T. H. Nash, St. Paul's Cray, U.S. Pat. 1,140,181, May 18, 1915. Date of appl., July 24, 1914.

SEE Eng. Pat. 6876 of 1914; this J., 1914, 610.

*Production of new compounds of unsaturated hydrocarbons, and of solutions and compositions containing the same.* Eng. Pat. 11,635. See XIII.

## VI.—BLEACHING; DYEING; PRINTING; FINISHING.

*Primuline; Dyeing with —, and substantive cotton dyeing.* R. Haller. *Färber-Zeit.*, 1914, 25, 301, 321. *Chem.-Zeit.*, 1915, 39, Rep., 98.

ULTRAMICROSCOPIC examination of a Primuline solution shows that the dyestuff is present in particles of very different degrees of dispersity. The particles showing the highest degree of dispersity pass through a membrane, and give the dialysate an intense blue fluorescence; this portion shows no dyeing properties, but recovers them on addition of electrolytes or on evaporation. Other substantive dyestuffs, e.g., Diamine Pure Blue, Congo, and Chrysophenine, show the same behaviour, but this is not the case with Carbazole Yellow and Cotton Yellow. The following explanation of substantive dyeing, based on Nägeli's micellar theory, is suggested: on introducing material into the dye-bath, the fibres are penetrated by the finely dispersed particles of dyestuff, and at the same time adsorption occurs, which soon prevents further penetration of the fibre by the highly dispersed particles of dyestuff. Addition of electrolytes, such as salt, leads to a decrease in the degree of dispersity to a stage at which the dyeing properties again make their appearance; at the same time some flocculation takes place. This view accounts for the fact that substantive dye-baths are never completely exhausted.—F. W. A.

*Fastness of dyeings to light; Improvement of the —.* K. Gebhard. *Färber-Zeit.*, 1914, 25, 393, 405. *Chem.-Zeit.*, 1915, 39, Rep., 87.

THE fastness to light of a dyestuff is not an absolute property, but is dependent in a high degree on the substratum. Malachite Green dyeings on cotton mordanted with Turkey red oil fade during the first week of exposure to light; on cotton mordanted with tannin and tartaremetic, in the middle of the second week; on wool and on cotton mordanted with tannin and tartar emetic, after-treated with thiourea, after more than eight weeks; and after-treated with sodium metaphosphate and glucose or with ammoniacal copper oxide and Turkey red oil, or as lake, after more than twelve weeks. The photochemical alteration of dyestuffs is considered to be due to an autoxidation process resulting in the formation of very labile dyestuff peroxide hydrates, which are stabilised by urea, and better by thiourea. The reactivity of the dyestuff may be destroyed by suitable methods of dyeing or after-treatment. The groups which become reactive in light may be made inactive by substitution or condensation with suitable substances, or by suitable after-treatment with metallic salts, hydroxy-acids, urea, thiourea, sodium molybdate, phosphotungstate, phosphite, metaphosphate, thio-sulphate, or nitrite.—F. W. A.

*Absorption [of dyes, alkaloid salts, etc.] from aqueous solution.* Freundlich and Poser. See IV.

*Electrical excitability and conductivity of liquid insulators [benzene, light petroleum, etc.]. Influence of soaps of naphthenic acids and of phenols on the electrical conductivity of heavy hydrocarbon oils.* Holde. See IIA.

### PATENTS.

*Alkali-free detergent for scouring and dyeing.* J. Barrington, Boston, Mass. U.S. Pat. 1,139,326, May 11, 1915. Date of appl., June 2, 1911.

A NEUTRAL vegetable oil soap, e.g., a coconut oil soap, is boiled with sulphonated castor oil and water until dissolved, a solution of an aniline

colour, adapted to dye both vegetable and animal fibres, is added, and the mixture boiled.

—H. R. D.

*Bleaching of cotton, artificial silk, and other goods; Process for —.* A. Lehmann. Ger. Pat. 279,993, Oct. 5, 1913.

COTTON, artificial silk, half-silk (artificial silk and cotton), jute, ramie, hemp, sisal, half-linen, wood, and muslin are bleached with bleaching powder or electrolytic bleach solution to which has been added malt or malt preparations (diastafor) to increase the activity of the solution, and hence effect bleaching in half the time with half the usual amount of bleaching agent.—F. W. A.

*Vat preparations; Process for producing concentrated —.* Farb. vorm. Meister, Lucius, und Brüning. Ger. Pat. 281,353, Sept. 19, 1913. Addition to Ger. Pat. 251,569.

IN addition to the extraordinary solvent action exerted by Turkone oil, Monopole soap, etc., on concentrated alkali salts of leuco-compounds of halogenated indigo or indigoid dyestuffs, these substances have been found to exert the same effect on the corresponding compounds of the quinone vat dyestuffs. Anthraquinone vat dyestuffs, such as Indanthrene, do not behave in this manner. The solutions obtained have many advantages over the coarse paste, which is difficult to reduce, and may be used direct by the wool dyer, alone or in combination with an indigo or other vat.—F. W. A.

*Multicolour effects in spun yarn or textile goods; Production of —.* A. Heinzel, jun. Ger. Pat. 280,369, Mar. 27, 1914. Addition to Ger. Pat. 277,497 (this J., 1915, 223).

IN carrying out the process described in the main patent, an alkaline bath not containing an oxidising agent is used, and the cerium compounds deposited on the artificial fibres are oxidised by air or other oxidising agent only after the fibres have been spun or spun and woven. The artificial fibres, after being impregnated with the cerium salt solution, may be treated with a vegetable or animal oil or fat, saponified or emulsified with alkali; the soap or emulsion may be applied simultaneously with the gelatin finish mentioned in the chief patent. The spun yarn or tissues made from the treated fibres are dyed at the lowest practicable temperature, for example 20° C.—F. W. A.

*Dyeing apparatus; Spools and like tubular supports for use in —.* J. G. Masson, Woonsocket, R.I., U.S.A. Eng. Pat. 18,500, Aug. 10, 1914.

SEE U.S. Pat. 1,120,398 of 1914; this J., 1915, 75.

## VII.—ACIDS; ALKALIS; SALTS; NON-METALLIC ELEMENTS.

*Lactic acid; Analysis of —.* L. Balderston. J. Amer. Leather Chem. Assoc., 1915, 10, 242—251.

THE following methods are recommended for adoption by the American Leather Chemists' Association. Volatile acid is determined by the distillation of a solution containing approximately 15 grms. of lactic acid per litre. A long-necked 300 c.c. flask fitted with a vertical condenser is used, the total height from the top of the condenser to the bottom of the flask being 20—24 inches. 150 c.c. of the dilute acid is distilled so that 125 c.c. of distillate comes over in 47 to 53 mins., the residue is diluted with 125 c.c. of water, and the distillation repeated. The two distillates are united, titrated with N/2 sodium hydroxide, and the result calculated to acetic acid.

To estimate free sulphuric acid, 50 grms. of the sample is dissolved in neutral 95% alcohol, the solution heated to 60°C., and allowed to stand over-night in a warm place. The solution is filtered, and the residue washed with alcohol. After evaporating the alcohol, the filtrate is diluted with water, and acidified with hydrochloric acid. Sulphuric acid is estimated in the usual way. Anhydride is determined by Besson's method (this J., 1910, 440). After titrating for total free acid, a further amount of  $N/2$  sodium hydroxide is added and the solution allowed to stand for 15 mins. A definite excess of  $N/2$  sulphuric acid is added, and the solution is heated to boiling and titrated back with alkali. The alkali used by anhydride is found by subtraction and calculated to lactic acid. Methods by which the solution is heated with the excess caustic soda give too high results for anhydride.—F. C. T.

*Formic acid formation; Chemical kinetics of —.*  
G. Bredig. *Z. Elektrochem.*, 1914, 20, 489—494.  
*J. Chem. Soc.*, 1915, 108, i, 211—212.

The formation of formates by the action of carbon monoxide on strong bases such as sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, and tetra-ethylammonium hydroxide at 50°—80°C. and pressures up to 40 atmos., was studied and also the action on weak bases such as piperidine, diethylamine, and isobutylamine. In all cases satisfactory figures can be obtained only if the reaction constant is calculated on the hypothesis that both hydroxyl ions and undissociated bases are concerned in the reaction. The constant for the action of the hydroxyl ions,  $k_{OH}$ , is independent of the nature of the base, the following figures being obtained for  $k_{OH}$  at 80°C.: NaOH, 0.0684; KOH, 0.0690;  $N(CH_3)_4OH$ , 0.0730;  $Ba(OH)_2$ , 0.0720; piperidine, 0.0810; diethylamine, 0.0730; and isobutylamine, 0.0710. If  $k_m$  represents the reaction constant of the undissociated molecules, then the ratio  $k_m:k_{OH}$  for the bases investigated is given by the figures KOH, 2.2;  $N(CH_3)_4OH$ , 1.9; NaOH, 1.1;  $Ba(OH)_2$ , 0.68; piperidine, 0.0030; diethylamine, 0.0045, and isobutylamine, 0.0026. The results show that with strong bases the action of the hydroxyl ions and undissociated molecules is of about the same dimensions, whereas with weak bases the action of the undissociated molecules is very much less.

*Sulphuric acid and potassium, especially in potash salts; Determination of —.* W. Vaubel. *Z. öfentl. Chem.*, 1914, 20, 426—434; 1915, 21, 1—6. *Z. angew. Chem.*, 1915, 28, Ref., 159.

THE author recommends determination of the sulphuric acid by the benzidine method and of potassium by the cobaltinitrite method. The acid sulphate solution is diluted till it contains 0.1—0.2%  $H_2SO_4$ , and precipitated with an equal volume of a solution of benzidine hydrochloride prepared by dissolving 0.7 grms. of the base in 20 c.c. of hydrochloric acid of sp. gr. 1.12, and diluting to 1 litre. The solution should not contain more than 10 mols. HCl, 15 mols.  $HNO_3$ , 20 mols.  $(H_2CO_3)_2H$ , 5 mols. alkali salts, or 1—2 mols. ferric iron per mol.  $H_2SO_4$ ; when one or more atoms of sulphur are present per atom of ferric iron, reduction to the ferrous state is not necessary. For the determination of potassium Zaleski's method (see this J., 1914, 1172) is recommended, using a reagent prepared by pouring a solution of 30 grms. of cobalt nitrite in 1 litre of water and 250 c.c. of nitric acid of sp. gr. 1.2 into a solution of 300 grms. of sodium nitrite in 1 litre of water, the mixture being agitated, allowed to stand for 24 hours, and filtered.—A. S.

*Calcium chloride; Importation of — into India.*  
Board of Trade J., June 3, 1915.

NOTIFICATION No. 3950—28 (Customs Circular No. 5 of 1915), dated 15th April, states that the Government of India have sanctioned the proposal to exempt calcium chloride from the payment of Customs duty, when imported by the owner of a cotton weaving mill and shown to the satisfaction of the Collector of Customs to be intended for use in the weaving of cotton or the baling of woven cotton goods. The above sanction is subject to reconsideration after the war.

*Phosphoric acid in limestone; Concentration method for the determination of small quantities of —.*  
F. Hinden. *Z. anal. Chem.*, 1915, 54, 214—216.

TWENTY-FIVE grms. of the powdered limestone is mixed with 100 c.c. of water and 120 c.c. of dilute nitric acid (1:1), the mixture is boiled for 10 mins., and the insoluble portion then collected on a filter and washed. The filtrate is heated to boiling and ammonia is added until the solution just becomes turbid owing to the precipitation of iron and aluminium hydroxides (if the limestone does not contain iron or aluminium compounds, a small quantity of ferric chloride should be added); 0.5 gm. of calcium carbonate is now added, the mixture boiled for 5 mins., and the precipitate, consisting of calcium carbonate, ferric carbonate, and aluminium hydroxide, and containing the whole of the phosphoric acid, is collected, washed, dissolved in dilute nitric acid, and evaporated to dryness. Any silica which separates is filtered off, and the phosphoric acid is then determined in the filtrate by the molybdate method.—W. F. S.

*Carbon dioxide in minerals; Determination of —.*  
L. H. Borgström. *Z. anal. Chem.*, 1914, 53, 685—687. *J. Chem. Soc.*, 1915, 108, ii, 281.

IN the estimation of carbon dioxide in minerals, such as scapolite, etc., the addition of a small quantity of hydrofluoric acid to the hydrochloric acid used for the decomposition accelerates the rate at which the mineral is dissolved, and the carbon dioxide is evolved completely in about fifteen minutes. The results obtained are higher and more concordant than when hydrochloric acid is used alone; the hydrofluoric acid attacks the flask to some extent, but the same flask may be used for a considerable number of estimations.

*Calcium thiosulphate; Some reactions of — from the standpoint of the law of mass action and the phase rule.* R. Krcmann and H. Rodemund. *Monats. Chem.*, 1914, 35, 1061—1113. *Z. angew. Chem.*, 1915, 28, Ref., 147.

CALCIUM thiosulphate, obtained by Moud's process from the waste calcium sulphide of the Leblanc process, is usually converted into sodium thiosulphate by treatment with sodium carbonate or sulphate. An investigation of the reaction from the standpoint of the law of mass action showed that the maximum yields attainable are 2—3% lower than the theoretical yields, probably because the reacting salts are prevented from coming into effective contact by the precipitated calcium carbonate or sulphate. The yields were higher at 25°C. than at lower temperatures, and in some cases sodium sulphate gave better results than the carbonate. Attempts to use sodium nitrate instead of the carbonate or sulphate did not prove successful; below 20–22°C. the solid phase invariably consisted of silky needles of the triple salt,  $CaS_2O_3 \cdot Na_2S_2O_3 \cdot NaNO_3 \cdot 11H_2O$ , which decomposed into its components at higher temperatures.—A. S.

*Tartrates; An adulterant of crude and refined —.*  
P. Carles. *Ann. Falsif.*, 1915, 8, 125—128.  
THE calcium tartrate from wine lees, etc., is

frequently converted, in the manufacturing process, into potassium bitartrate by boiling with potassium bisulphate. The presence of calcium tartrate in the mixed tartrates is also sometimes masked by an addition of bisulphate. The addition may be detected by shaking the powder with 50% alcohol, when the filtrate will show excessive acidity and give a precipitate with barium chloride if bisulphate be present. To avoid an excessive quantity of water in the industrial extraction of potassium bitartrate, it is suggested that the material should be treated with sodium hydroxide solution, which will convert the sparingly soluble bitartrate into the readily soluble (100 in 120 of water at 15°C.) neutral tartrate of sodium and potassium. The alkaline solution is then treated with sulphuric acid to separate the bitartrate. If the material consists of the mixed tartrates of potassium and calcium, the process is reversed, the sulphuric acid being used first, and the acid solution neutralised with potassium hydroxide. Limits of 0.75% total sulphates as  $K_2SO_4$  and 0.25% of calcium sulphate are suggested for such bitartrate powders.—C. A. M.

*Cuprous carbonate.* P. Carles. Bull. Soc. Chim., 1915, 17, 163—164.

In the preparation of ammoniacal copper solution by circulating air and ammonia solution alternately through a tower containing copper, the metal becomes coated with blue cupric carbonate, which may be removed by violent agitation with water. When kept for several weeks in a stoppered flask in contact with the metal and ammonia solution, the cupric carbonate was reduced to cuprous carbonate, which is a sea-green powder insoluble in water or ammonia and fairly stable in air.—J. R.

*Carbon-free compounds; Optical activity of —.*  
*The asymmetric cobalt atom.* XII. A. Werner. Ber., 1914, 47, 3087—3094. J. Chem. Soc., 1915, 108, ii., 264—265.

AFTER many unsuccessful searches after purely inorganic compounds which exhibit optical activity, it has been found that the dodecamminehexol-tetracobaltihaloids,  $\{Co[(OH)_2Co(NH_3)_4]_3\}X_6$ , may be resolved by means of the silver bromocamphor-sulphonates. The active bromides were prepared by dissolving the bromocamphorsulphonates in just sufficient aqueous acetone (50%), adding small quantities of sodium bromide until the precipitate had a marked activity, and then diluting the mother liquor with absolute alcohol. The *d*- and *l*-bromides crystallised as reddish-grey powders with  $2H_2O$ . The salts exhibit most abnormal rotation-dispersion. The highest rotations observed were  $[\alpha]_{440} = +4440^\circ$  and  $-4500^\circ$  in 50% aqueous acetone.

*Sulphur; Formation of free sulphuric acid from —.* W. Zanker and E. Färber. Färber-Zeit., 1914, 25, 343, 361. Chem.-Zeit., 1915, 39, Rep., 110.

POWDERED sulphur always contains some free sulphuric acid, and cannot be completely freed from it by washing for days with cold or hot water. If cotton is impregnated with sulphur which has been precipitated from alkaline solutions, and is then repeatedly dried at  $140^\circ$ — $160^\circ$  C. and exposed to the air between these operations, it becomes superficially carbonised. The presence of a trace of sulphuric acid in sulphur accelerates the formation of further quantities.—J. H. L.

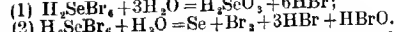
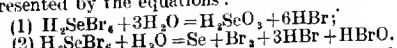
*Sulphur molecule; A third and fourth variety of —.*  
*IV. Engel's sulphur.* A. H. W. Aten. Z. physik. Chem., 1914, 88, 321—379. J. Chem. Soc., 1915, 108, ii., 254—255. (See also this J., 1914, 1087.)

In addition to  $S_8$ , ordinary rhombic sulphur, and  $S_6$ , insoluble amorphous sulphur, two other

varieties of sulphur exist which are different from the foregoing either in molecular size or in molecular constitution.  $S_7$  is formed when sulphur is heated above its melting point and then rapidly cooled, or by warming solutions of  $S_8$  in sulphur chloride; in other solvents, such as carbon bisulphide, the rate of formation of  $S_7$  from  $S_8$  is very slow. Solutions of  $S_7$  differ from solutions of  $S_8$  in their strong yellow colour.  $S_6$  (Engel, this J., 1891, 639) is obtained when a strong solution of hydrochloric acid at  $0^\circ$  C. is added to a cold solution of sodium thiosulphate and the aqueous solution shaken with toluene. From the toluene solution  $S_6$  crystallises after a short time. It is characterised by its orange-yellow colour, and also by its crystal form. Its solutions are yellow, but not so strongly coloured as those of  $S_7$ . The difference of  $S_7$  and  $S_6$  is definitely proved by the solubility of the two forms.  $S_8$  is  $S_8$ ,  $S_6$  is  $S_6$ ,  $S_7$  is probably  $S_7$ . Solutions of  $S_7$  and  $S_6$  are stable in the dark, but the addition of  $S_8$  causes a separation of  $S_8$ . The quantity of  $S_8$  which separates is proportional to the quantity of  $S_8$  added and to the quantity of  $S_7$  and  $S_6$  present in the solution. The deposition takes place more slowly at  $0^\circ$  than at  $25^\circ$  C., and is slower from a solution of  $S_6$  than from one of  $S_7$ . The separation is much slower from carbon bisulphide than from toluene solutions.  $S_7$  and  $S_6$  are converted partly into  $S_8$  and partly into  $S_4$  on shaking their solutions with potassium hydroxide solution. The same change occurs with ammonia, and the change takes place four times as quickly with  $S_6$  as with  $S_7$ . If a solution of ammonia in toluene is used, practically no  $S_8$  is formed, but only  $S_4$ . Solid  $S_6$  changes slowly in the dark and more rapidly in the light into  $S_4$  and  $S_8$ ; the amount of  $S_4$  formed is practically the same in both cases, but the amount of  $S_8$  is much greater in the light. When a solution of  $S_6$  is submitted to light, a small deposition of  $S_8$  occurs, but no formation of  $S_4$ . On the other hand  $S_7$  is rapidly converted into  $S_8$  on being submitted to light. The density, viscosity, and refractive index of solutions of  $S_8$ ,  $S_7$ , and  $S_6$  differ only slightly from one another. On allowing the three forms to act on silver and mercury,  $S_8$  acts most rapidly and  $S_6$  more slowly, and the presence of  $S_7$  retards the action of  $S_8$ . During the action on the metals,  $S_6$  is transformed into  $S_8$ , and  $S_7$  into  $S_8$ , but more slowly.

*Selenium; New method for the preparation of colloidal —.* A. Guthrie and F. Engeroff. Kolloid. Zeits., 1914, 15, 193—201, 210—218. J. Chem. Soc., 1915, 108, ii., 255—256.

THE decomposition of hydrogen selenium hexabromide,  $H_2SeBr_6$ , by water may be conveniently employed in the preparation of a colloidal solution of selenium. Hydrogen selenium hexabromide is obtained by adding bromine slowly to a mixture of finely divided selenium and hydrobromic acid of sp. gr. 1.45, which is kept cool during the reaction. On keeping for some hours, the hexabromide separates in the form of dark red crystals, which dissolve in hydrobromic acid, forming a solution which is quite stable in the absence of light. On dilution of this solution, selenium separates in a colloidal form. The changes taking place may be represented by the equations:



The colloidal solution of selenium thus obtained may be purified by dialysis. By the addition of 1% of gum arabic its stability is greatly increased.

*Monazite sands of Travancore.* G. H. Tipper. Rec. Geol. Survey, India, 1914, 44 [3]. Ch. of Comm. J., 1915, 34, 205.

MONAZITE is widely distributed over the state of

Travancore, but there are only a few places where concentration has given rise to deposits of sufficient richness to be called monazite sands. These places are all in the vicinity of the sea-coast. No concentrates seem to occur in any of the rivers. The deposits are usually black, due to the presence of magnetite and ilmenite. They are sometime red when garnets are in excess. Where there is abundance of quartz or calcite, a grey sand is produced. Excess of monazite gives a yellowish tinge. The monazite occurs as small rounded grains varying from 0.1 to 0.2 mm. in diameter. In colour it resembles amber, and its specific gravity is 5.191. A specimen free from zircon or any other mineral likely to complicate the analysis was found to contain 6.0% of thorium. In other analyses the amounts of thorium present in two samples of magnetically separated sand were respectively 8.5 and 10.08%, whilst other tests gave 10.22 and 8.65% of thorium in two samples of Travancore monazite, isolated from concentrates.

**Radium D; Preparation of**—in visible amounts, and its chemical identity with lead. G. von Hevesy and F. Paneth. Ber., 1914, 47, 2784–2786. Chem.-Zeit., 1915, 39, Rep., 134.

THE emanation from 1 gm. of elementary radium was sealed up in a quartz tube; after several weeks, during which the emanation decayed, the contents of the tube were washed out with nitric acid. The resulting solution upon electrolysis yielded either radium D or its peroxide. Radium D thus obtained was chemically identical with inactive lead, and if both are present in a solution the sum of the two concentrations must be used in applying the law of mass action.—J. R.

**Radio-elements; Adsorption and precipitation of the**—F. Paneth. Physikal. Zeits., 1914, 15, 324–329. J. Chem. Soc., 1915, 108, ii., 205–206. (See this J., 1915, 281.)

IN N/1 hydrochloric acid barium sulphate adsorbs 88% of radium sulphate, but silver chloride does not adsorb radium chloride at all.

**German Potash Syndicate; Sales of the**—Pharm. J., June 12, 1915. (See also this J., 1915, 175, 352, 422.)

SINCE the prohibition of exports two or three months ago, the oversea export trade has entirely ceased, but the embargo does not affect deliveries to Austria-Hungary. Deliveries have also been permitted to Scandinavia and Holland and to Italy to a limited extent for a time until they were finally discontinued. The result of the veto on the export trade is shown by the circumstance that, as contrasted with the first four months in 1914, the total exports in the same months this year have declined from £1,226,000 to £2,187,000.

#### PATENTS.

**Hydrochloric acid and normal potassium sulphate; Production of**—from sodium bisulphate and potassium chloride. Gewerkschaft Andie. Ger. Pat. 282,253, Sept. 19, 1913.

SODIUM bisulphate is converted into potassium-sodium sulphate by roasting with more than the theoretical quantity of potassium chloride, and the double salt is converted into potassium sulphate by dissolving it in water, or preferably in a dilute solution from another stage of the process, and treating the solution with excess of potassium chloride; the solution should contain 70–75 grms.  $\text{Na}_2\text{SO}_4$  per litre.—A. S.

**Acetic acid; Process for the concentration of dilute**—Akt.-Ges. f. Anilinfahr. Ger. Pat. 282,263 Jan. 25, 1914.

CONCENTRATED acetic acid is obtained by distilling the dilute acid with metaphosphoric acid. The residue is reconverted into metaphosphoric acid by heating.—F. W. A.

**Potash salts; Apparatus for the continuous decomposition and dissolving of**—R. Fleischer. Ger. Pat. 282,252, June 1, 1913.

THE apparatus comprises a fixed trough along the bottom of which extends a shaft provided with helical agitating blades. The devices for lifting the solid material consist of trough-shaped pieces fixed between adjacent agitating blades at an angle to the shaft, so that the material lifted is discharged in the direction of movement of the solution through the trough. The shaft is hollow and serves as an inlet main for a heating agent, which passes to sets of heating tubes arranged parallel to the shaft and connected with it by straight or curved connecting tubes.—A. S.

**Crystallisation of hot-saturated saline solutions, especially solutions of potassium salts.** G. Sauerbrey Maschinenfabr. A.-G. Ger. Pat. 282,506, Aug. 30, 1913. Addition to Ger. Pat. 271,240 (this J., 1914, 484).

AIR from the ventilating shafts is used as cooling agent.—A. S.

**Alkali chlorides; Apparatus for electrolysis of**—K. Ochs, Berlin-Charlottenburg, Assignor to Siemens und Halske A.-G., Siemensstadt, Germany. U.S. Pat. 1,138,400, May 4, 1915. Date of appl., Nov. 13, 1914.

A CONTAINING vessel fitted with a horizontal porous diaphragm has positive electrodes above, and negative electrodes below the diaphragm. Vertical partitions, adjacent to the upper surface of the diaphragm and submerged in the liquid between it and the positive electrode, are of such a height and distance apart that bodily motion of the liquid near the diaphragm is prevented.—F. SODX.

**Sodium silicate; Process of dissolving**—W. H. Stanton and J. G. Vail, Chester, Pa., Assignors to Philadelphia Quartz Co. U.S. Pat. 1,138,595, May 4, 1915. Date of appl., March 6, 1913.

WATER is heated with an excess of substantially anhydrous sodium silicate in a vessel surrounded with steam, in such manner that circulation of the liquid is minimised and retardation of solution by hydrolysis prevented.—F. SODX.

**Sodium bisulphite crystals; Drying**—H. Howard, Brookline, Mass. U.S. Pat. 1,138,658, May 11, 1915. Date of appl., June 24, 1913.

THE wet crystals are heated and agitated in a current of hot sulphur dioxide gas passing through a closed chamber. The moisture from the effluent gas is removed and condensed, and the gas again returned to the chamber after heating.—H. R. D.

**Sand; Process for bleaching**—J. G. A. Rhodin, London. Eng. Pat. 8495, April 3, 1914.

SAND, discoloured by iron compounds or the like, is mixed with about 24% by weight of common salt in a moist state and heated in a furnace to 1100°–1200° C. for one or two hours. After cooling, the mass is lixiviated.—H. R. D.

**Aluminate solutions; Process of treating**—H. Howard, Brookline, Mass. U.S. Pat. 1,137,860, May 4, 1915. Date of appl., May 24, 1913.

SILICA is removed from the solution by diluting it until the concentration does not exceed 30° B.

(sp. gr. 1.263) and subjecting the hot liquid to the action of the residues from the treatment of bauxite with alkali. Aluminium hydroxide may be produced by digesting bauxite with an alkaline aluminate solution, diluting the resulting liquid, and removing silica by further heating in presence of the undissolved residue.—H. R. D.

*Zinc chloride solutions; Method of treating ferruginous* — S. H. Lawton, Assignor to American Vulcanized Fibre Co., Wilmington, Del. U.S. Pat. 1,137,871, May 4, 1915. Date of appl., June 21, 1913.

A PRECIPITANT for iron is introduced into zinc chloride solutions containing dissolved ferric salts (the iron being in excess of 1% of the zinc), and the solution is concentrated until the precipitate is converted into anhydrous ferric oxide. Claim is also made for a method of dehydrating ferric compounds by treatment with concentrated zinc chloride solutions.—H. R. D.

*Nitrogen; Process for fixing atmospheric* — J. E. Bucher, Coventry, R.I., Assignor to Nitrogen Products Co., Providence, R.I. U.S. Pat. 1,138,190, May 4, 1915. Date of appl., July 17, 1913.

A MIXTURE of nitrogen and the vapour of an alkali or alkaline-earth metal is brought into intimate contact with a heated mass of catalytic material containing carbon in solution, so as to form a cyanogen compound of the metal, and fresh carbon is supplied to the catalytic surface as the amount in solution is diminished by the reaction.—F. SODN.

*Ammonia and the like; Method of producing* — J. E. Bucher, Coventry, R.I., Assignor to Nitrogen Products Co., Providence, R.I. U.S. Pat. 1,138,191, May 4, 1915. Date of appl., Jan. 8, 1914.

NITROGEN is brought into contact with a mass of catalytic material (e.g., a metal) containing carbon in solution, which is heated to about 725° C. The dissolved carbon combines simultaneously with the nitrogen and with a metal present as the base of an oxy-compound, to form a cyanogen compound, which immediately reacts with steam to give ammonia and the metallic oxy-compound again.—F. SODN.

*Base-exchanging substances; Method of manufacturing* — R. Gans, Grünwald-Berlin, Germany. U.S. Pat. 1,140,262, May 18, 1915. Date of appl., Oct. 27, 1913.

SEE Eng. Pat. 1039 of 1914; this J., 1914, 549.

*Calcium cyanamide; Process of producing* — Dettifoss Power Co., Ltd., and J. H. Lidholm, London. Eng. Pat. 3545, Feb. 11, 1914. Under Int. Conv., Feb. 18, 1913.

SEE Fr. Pat. 469,045 of 1914; this J., 1914, 962.

*Purification of coke-oven gases and waste liquors containing salts of heavy metals*. Ger. Pat. 280,849. See 11A.

*Method of operating an electrolytic cell [for the production of chlorine]*. U.S. Pat. 1,139,389. See XI.

### VIII.—GLASS; CERAMICS.

*Glass suitable for X-ray bulbs; Soft soda* —

The Glass Research Committee of the Institute of Chemistry find that a glass such as that made from formula No. 10, recently published (see this J., 1915, 424), and recommended for X-ray bulbs,

does not give a green phosphorescent glow, but a slight blue glow, if it is made from approximately pure materials. The green phosphorescence preferred by users of X-ray tubes, is due to the presence of manganese, and such a glass as No. 10 will give this green glow if manganese dioxide is added to the batch mixture in the quantities frequently used to correct the colour due to iron.

*Clay and kaolin suspensions; Action of alkali silicates on* — P. Rohland. Kolloid. Zeits., 1914, 15, 158—159. J. Chem. Soc., 1915, 103, ii., 240.

IF a small quantity of a solution of an alkali silicate is added to a suspension of raw kaolin, the particles of quartz and sand separate out very quickly. Various observations show that this cannot be attributed to the influence of the colloidal silicic acid or the hydroxyl ions which are formed as a result of the hydrolysis of the silicate, but must be ascribed to the action of the undissociated alkali silicate in the colloidal state. This action results in an increase in the degree of dispersity of the kaolin particles, and the settling out of the quartz and sand particles is a consequence of this physical change.

*Adsorption capacity of talcs and kaolins [for dyes]*. Rohland. See IV.

### PATENTS.

*Glass articles; Machines for working and blowing* — J. Gray, London. From Empire Machine Co., Portland, Me., U.S.A. Eng. Pat. 9452, April 16, 1914.

THE machine is constructed to gather a variable quantity of glass on the blow rod and automatically to chill the glass locally by means of a groove, so that only the requisite amount of glass is permitted to elongate for the final blowing. Any superfluous glass of the gather may be forced back on the blow rod so that it does not enter into the production of the finished article. One or more marverers and grooving blocks and a gauge cup are moved mechanically in proper sequence into contact with the gather on the rod. The faces of the marvering blocks are inclined to the axis of the rod. A mechanically driven carrier holds the gather on the blow rod in a fixed relation to the marvering device, and both are rotated in unison.—W. C. H.

*Glass-melting tank-furnace*. G. E. Howard, Butler, Pa., Assignor to The Pittsburgh Plate Glass Co., Pittsburgh, Pa. U.S. Pats. (A) 1,138,110 and (B) 1,138,111, May 4, 1915. Dates of appl., Aug. 15 and Nov. 15, 1913.

(A) THE melting tank is in constant communication with a chamber provided with a discharge opening. A hood is arranged within the chamber and communicates freely with it, so that normally the height of the glass is the same in the tank, chamber, and hood. The opening between the tank and the chamber is smaller than that between the chamber and the hood, in order to oppose the return of the glass from the chamber to the tank. An air suction and pressure apparatus is connected with the hood, by which the glass in the hood can be sucked up above its normal level and then by the air-pressure can be caused to flow more rapidly out of the discharge opening. (B) A separate delivery reservoir is combined with a stationary glass-melting tank, and has a discharge opening which can be moved or tilted from a position on a level with the glass in the tank to a point below that level. Glass is transferred from the tank to the delivery reservoir by a siphon. The siphon connection can be broken when the delivery reservoir requires cleaning or repairing. Means are provided for regulating the height of glass in the siphon, which

is of sufficient sectional area to convey more glass in a given time than would be melted in the tank, in order to maintain the level of the glass in the delivery reservoir during the discharging period.

—W. C. H.

*Glass-drawing apparatus.* H. F. Hitner, Mount Vernon, Ohio, Assignor to The Pittsburgh Plate Glass Co., Pittsburgh, Pa. U.S. Pat. 1,133,870, May 11, 1915. Date of appl., July 6, 1911. Renewed Oct. 15, 1914.

THE glass-drawing apparatus is combined with a furnace which has a vertically movable top stone, provided with a glass-drawing opening. One or more cables are attached to the top stone, the upper ends of the cables being secured to a lateral arm connected to a crank which can be rotated by suitable means. The throw of the crank is adjusted to give the required range of movement to the top stone, which is lifted during one half, and lowered during the other half of the forward rotation of the crank. An indicator, actuated by the rotation of the crank, gives a signal when the top stone reaches its lower position. The cover of the top stone is provided with two cables, one of which extends vertically upwards, and the other diagonally upwards towards the side to which the cover is to be shifted. The upper ends of these cables are fastened to a pair of cranks, so that during one half of the rotatory movement of the cranks, the cover is raised and shifted laterally, and during the other half of the movement it is shifted back to position over the top stone.

—W. C. H.

*Kiln.* U.S. Pat. 1,139,327. See I.

*Process for bleaching sand.* Eng. Pat. 8495. See VII.

## IX.—BUILDING MATERIALS.

*Concrete ; Permeability tests of* — M. O. Withcy. Western Soc. Engineers (U.S.A.), 1914. Engineering, 1915, 99, 589—592.

DETAILS are given of an investigation made with 294 specimens of concrete composed of Portland cement, pit sand, and gravel in the proportions of 1:1½:3, 1:2:4, and 1:3:6 by volume and 1:5, 1:7, and 1:9 (cement:aggregate) by weight. Three forms of test-piece were used, that most commonly employed consisting of a cylindrical concrete core surrounded by a shell of 1:1 mortar, both cast at the same time. Mixing was effected mechanically and by hand, and the specimens were tested by means of water under air-pressures up to 43 lb. per sq. in. Permeability decreased rapidly with the age of the specimens for the first month, after which the change was slight. Specimens in which the weight ratio of cement to aggregate exceeded 1:9 exhibited no visible sign of dampness at pressures less than 40 lb. per sq. in.; but, with the same method of mixing and curing, impermeability was not increased proportionately when the weight ratio was raised to more than 1:7. To produce good concrete it was found important to grade the sand and gravel into different sizes and re-combine these to obtain the maximum density; most of the more impervious mixtures used in the tests contained 40—46% of fine material, and impermeability generally increased with density. Concrete, 1:9 by weight and practically impervious to water at pressures below 40 lb. per sq. in., was obtained by using sand and gravel graded in accordance with Fuller's curve (Trans. Amer. Soc. Civil Eng., 1907, 59, 67), but required special care in manufacture and curing. With 1:1½:3 concrete,

the time of mixing (¾ to 5 mins.) had no effect on permeability, but with 1:3:6 concrete, greater strength and impermeability were obtained by mixing for 2 than for ¾ or 5 mins. in a No. 0 Smith mixer run at 28—30 revs. per min. As showing the effect of consistency on permeability, mixtures which would barely flow were the most efficient, especially in the case of lean concretes; density and impermeability were decreased by the use of too much water, but an excess of the latter was less harmful than too little. Permeability was most affected by the method of curing: the average leakage through concrete air-dried for 27 days after setting, was 140 times that through similar specimens sprinkled with water for the same period; and it was found advisable, in the case of sections up to 6 or 8 in. thick, to keep the set concrete damp for a month if lean and for at least two weeks if rich. The permeability of properly cured, lean concrete was increased by complete desiccation, but rich concrete was not much affected. Lean concrete appeared to be less permeable in the direction of pouring than normal to this direction. Although none of the concretes tested was absolutely water-tight (if continuous flow into the specimens be taken as evidence of permeability), the majority were practically so, since no visible evidence of flow appeared. In nearly all the 1:7 or richer mixtures employed, the rate of flow for a period of 54 hours at a pressure of 40 lb. per sq. in. was less than 0.0001 U.S. gallon per sq. ft. per hour, the minimum flow for which leakage was visible being 0.0001 U.S. gallon per sq. ft. per hour.—W. E. F. P.

## PATENTS.

*Porous substances [wood] ; Process for coating* — J. W. Aylsworth, East Orange, Assignor to Condensite Co. of America, Glen Ridge, N.J. U.S. Pat. 1,139,470, May 18, 1915. Date of appl., April 10, 1912.

WOOD is dried for several hours at 220° F. (105° C.), and coated, while hot, with a mixture of "a phenol resin, a methylene-containing hardening agent, and a substance adapted to render the mass fluid at a relatively low temperature," the mixture being at a lower temperature than the wood. The coated wood is baked below 220° F. until the coating is converted into a hard, infusible product.—W. E. F. P.

*Wood-preservative.* J. A. De Cew, Montreal, Canada. U.S. Pat. 1,140,127, May 18, 1915. Date of appl., June 25, 1913.

SEE Eng. Pat. 5411 of 1912; this J., 1913, 535.

## X.—METALS; METALLURGY, INCLUDING ELECTRO-METALLURGY.

*Foundry pig iron ; Export of* — Board of Trade J., June 3, 1915.

THE War Trade Department notifies that arrangements have been made whereby the prohibition against the export of foundry pig iron from the United Kingdom will in future be regarded as including only such foundry pig iron as contains (1) less phosphorus than 0.1%, or (2) less silicon than 1.5% together with less sulphur than 0.09%. It is proposed that certificates to the effect that the foundry pig iron is of a quality which may be exported without licence shall be issued by either of the two following committees:—(1) representing the Cleveland Iron Masters' Association (Secretary, Mr. J. T. Atkinson); (2) representing the Scottish Iron Masters' Association (Secretary, Mr. J. C. Bishop).



*Iron alloys; Thermo-electric force of certain —.* T. S. Fuller. Amer. Electrochem. Soc., April, 1915. Met. and Chem. Eng., 1915, 18, 318—319.

THE results of the measurement of the thermo-electromotive force of certain iron alloys against copper for the interval 0°—100°C. are given in millivolts in the table.

Iron-nickel.			Iron-chromium.			Iron-cobalt.		
Fe	Ni	E.M.F.	Fe	Cr	E.M.F.	Fe	Co	E.M.F.
100	—	+0.36	90	10	1.20	90	10	—0.64
83	17	—0.64	82	18	1.04	80	20	—3.70
80	20	—0.55	80	20	0.43	70	30	—3.50
70	30	—0.52	76.5	23.5	0.32			
18.8	81.2	—2.45						
7	93	—1.90	70.5	29.5	0.31			
—	100	—2.38						

Iron-nickel-chromium.				Iron-nickel-manganese.			
Fe	Ni	Cr	E.M.F.	Fe	Ni	Mn	E.M.F.
73	17	4	—0.12	87	10	3	—1.09
70	20	10	—0.46	86	12	2	—1.02
33	53	10	0.00	81	17	2	—1.50
25	60	15	0.07	80	17	3	—0.79
25	50	20	0.07	76.5	17.5	6	—0.73
20	55	25	—0.08	76	22	2	—1.84
4	89.6	5.65	1.70	50	44	6	—0.59

—W. R. S.

*Steels; Hardness and brittleness of —.* Grand. Int. Zeits. Metall., 1914, 5, 179—185. Chem. Zeit., 1915, 39, Rep., 71.

IN determining hardness by the Brinell method, when a load of 3000 kilos. is used, the surface of the indentation produced by the ball may not be smooth, and it will then be necessary to measure the height of the protuberance in order to ascertain the true surface area of the indentation. For exact work the load should be applied for at least 5 mins. The ratio of the Brinell hardness number to the tensile strength does not vary much for carbon steels, ranging from 0.318 to 0.360 according to the composition and previous heat treatment of the steel. Some indication of the nature of the previous heat treatment may be gained by comparing the hardness numbers of a test specimen before and after annealing.—A. S.

*Passivity of iron; Influence of substances of different chemical nature on the —.* F. Flade and H. Koch. Z. physik. Chem., 1914, 88, 307—320. J. Chem. Soc., 1915, 108, ii., 218—219.

WHEN an iron electrode is placed in a N/10 sulphuric acid solution and anodically polarised, a stationary condition sets in, in which a constant current passes, and the iron has a definite potential. If now the polarising potential is gradually changed, the electrode potential suddenly falls at a definite point, the value which it reaches representing a sharp transition from the active to the passive condition (this J., 1911, 694). Strong surface-active substances (amyl alcohol, isobutyl alcohol, and isopropyl alcohol) are without influence on the stationary potential and the transition potential, from which it follows that the existence of the passive layer is independent of the surface forces. The addition of weak acids, including butyric, valeric, heptic, oxalic, malonic, succinic, benzoic, and phosphoric acids, causes the transition potential to move to the more positive side, that is, there is less tendency for the iron to become active in the presence of these acids. The oxidising agents, chromic acid and permanganic acid, either entirely prevent the iron from becoming active, or

by changing the transition potential render it less likely to become active. The reducing agents, sulphurous acid and phosphorous acid, tend to convert passive iron into the active form, whereas hydroxylamine, hydrogen sulphide, and hydrogen cyanide are without influence. Hydrogen peroxide increases the current strength at the stationary point, and thus acts as a reducing agent. This effect is at first strong, but decreases with time. Hydrogen peroxide causes the transition potential to move to the more positive side, and in this respect it behaves as an oxidising agent. The influence of halogen ions, added in the form of hydrochloric, hydrobromic, and hydriodic acids, is to cause passive iron to become active under conditions which normally would ensure its remaining passive. The change from passive iron to active iron in these cases is preceded by an induction period.

*Electrolytic and pure chemical processes; Relationship between —.* [Action of a mixture of sulphuric acid and hydrogen peroxide on metals.] D. Reichenstein. Z. Elektrochem., 1914, 20, 406—417. J. Chem. Soc., 1915, 108, ii., 245—246.

IN a previous communication it was shown (J. Chem. Soc., 1914, 108, ii., 23) that passivity of metals is analogous to those chemical reactions which, with increasing concentration of one of the reacting substances, at first show an increasing velocity of reaction, and then a steadily decreasing reaction velocity. A number of such reactions are considered in the present paper, and a mathematical representation of the rate of solution of metals in a mixture of sulphuric acid and hydrogen peroxide is deduced. It is shown that the action of such a solution on nickel is to be regarded as taking place in the four stages: (a) adsorption of hydrogen peroxide, (b)  $\text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{O}$ , (c)  $2\text{O} \rightarrow \text{O}_2$ , and (d)  $\text{Ni} + \text{O} + 2\text{H}^+ \rightarrow \text{Ni}^{++} + \text{H}_2\text{O}$ . The reaction b takes place slowly; its velocity is of the same order as that of c and d. The reaction c leads to the accumulation of oxygen in the electrode volume. With small concentrations of acid both b and c bring about a slowly increasing passivity of the metal. In a solution containing 0.970.N- $\text{H}_2\text{O}_2$  and 0.045.N- $\text{H}_2\text{SO}_4$  nickel becomes passive in ninety minutes, whereas in 0.423.N- $\text{H}_2\text{O}_2$  and 0.057.N- $\text{H}_2\text{SO}_4$  one hundred and seventy minutes is necessary. The constant velocity of solution of nickel, which is independent of the time, can also be reached from the passive side.

*Gold-platinum-palladium lode in Southern Nevada.* A. Knopf. J. Wash. Acad. Sci., 1915, 5, 370.

THE main ore shoot at the Boss gold mine, Clark Co., averages Au 3.46, Ag 6.4, Pt 0.70, and Pd 3.38 oz. per ton. The precious metals are associated with plumbogarsite,  $\text{Pb}[\text{Fe}(\text{OH})_6](\text{SO}_4)_2$ , pockets of this mineral carrying about 100 oz. Pd and Pt and several hundred oz. Au per ton. With the exception of the New Rambler deposit, Wyoming, this is the only important primary deposit in which platinum metals are constituents of predominant value.—W. R. S.

*Cyanide solutions; Notes on the practical testing of working —.* E. H. Croghan. J. Chem., Met., and Min. Soc., S. Africa, 1915, 15, 271—276.

THE results of the determination of free and total cyanide and alkalinity in a number of working solutions by different methods are tabulated, attention being called to the diversity of results obtained with solutions containing zinc. It is suggested that a uniform mode of testing be adopted.—W. R. S.

*Bornite as silver precipitant.* C. Palmer. J. Wash. Acad. Sci., 1915, 5, 351—354.

THE composition of a pure specimen of massive



bornite was found to correspond to the empirical formula,  $\text{Cu}_3\text{FeS}_4$ . The finely ground mineral was digested with silver sulphate solution, with which it reacted as follows:  $\text{Cu}_{15}\text{Fe}_2\text{S}_8 + 10\text{Ag}_2\text{SO}_4 = 10\text{Ag} + \text{Ag}_{10}\text{Fe}_2\text{S}_8 + 10\text{CuSO}_4$ . This proved that the whole of the copper was present in the cuprous state, and that the mineral has the constitution,  $5\text{Cu}_3\text{Fe}_2\text{S}_8$ .—W. R. S.

*Electric furnaces for re-heating, heat treatment, and annealing.* T. F. Baily. Proc. Eng. Soc. W. Pa., 1915, 31, 255—272.

THE advantages of electric over fuel furnaces for re-heating are: more accurate temperature control, non-oxidising atmosphere, saving in space, elimination of blast and stack, uniformity of temperature throughout the heating space, and smaller loss of heat. The thermal efficiency varies greatly with the size and capacity; a furnace of 60 kilowatts capacity heating 250 lb. of steel per hour to  $1200^\circ\text{C}$ . has an efficiency of 50%; in annealing work ( $900^\circ\text{C}$ .) a 600-kilowatt 3-ton furnace has an efficiency of 90%. Re-heating furnaces are constructed of fire-brick surrounded by insulating material within a steel shell. Foundry coke crushed to pea-size is used as resistor between the carbon electrodes; the metal to be heated is placed directly over the coke but not in contact with it. Electrically heated soaking-pits compare favourably with gas-fired ones as regards heating cost, and eliminate surface defects in the ingots as well as 2% metal loss due to oxidation. For heat-treating and annealing, the great advantage of the electric furnace lies in the accurate control and uniformity of temperature essential for securing uniform results from day to day. In the automatic continuous furnace the material, on reaching the required temperature at the discharge end, is tipped into the quenching-tank by mechanism controlled by a pyrometer.—W. R. S.

[*Or*] *flotation; Recent progress in —.* O. C. Ralston and F. Cameron. Eng. and Min. J., 1915, 93, 937—940.

IN American ore flotation plants the concentrates and tailings from the first "rougher" machines are usually re-treated in "cleaner" machines. Drag devices for removing froth from the tailing pulp are also much used. Froth in the concentrates may be broken up by spraying with water, but preferably the concentrates are passed direct into a pressure-filter. Mixed sulphide concentrates are run over tables after breaking the froth. Four American plants have adopted processes for selectively floating galena in presence of zinc blende (see Eng. Pats. 16,141 and 16,302 of 1913, and 9049 of 1914; this J., 1914, 869; 1915, 497). In the re-treatment of tailings a further quantity of oil is usually added. Pine oil, eucalyptus oil, or wood creosote is generally used for lead and zinc sulphides, and petroleum products for copper ores. The use of acid in the mill water often improves flotation by removing films of oxide, but in some cases may be harmful. A better grade of concentrate can often be obtained by heating to about  $50^\circ\text{C}$ . In Fields' process, flotation is caused by bubbles of hydrogen produced electrolytically in the pulp suspension. Experimental work is being done on the flotation of oxidised copper ores by converting them into sulphide by the action of soluble sulphides.—W. R. S.

*Arsenic; Separation of — from tungsten [vanadium, and molybdenum].* T. Dieckmann and S. Hilpert. Ber., 1914, 47, 2444—2446. Chem.-Zeit., 1915, 39, Rep., 121.

THE mass obtained by fusing the finely powdered tungsten, vanadium, or molybdenum ore with sodium hydroxide and sodium peroxide is extracted with water and the residue washed with dilute sodium hydroxide solution, after which arsenic is

determined by neutralising the concentrated filtrate and distilling with a mixture of phosphoric and hydrochloric acids.—J. R.

*Arsenic in lead; Determination of — by hypophosphorous acid.* L. Brandt. Z. öffentl. Chem., 1915, 31, 66—71. J. Chem. Soc., 1915, 103, ii, 280. (See this J., 1914, 28, 504.)

THE metal is dissolved in hydrochloric acid containing bromine, the excess is expelled by heating the solution, and, after cooling, 20 c.c. of hypophosphorous acid of sp. gr. 1.15 and 50 c.c. of concentrated hydrochloric acid are added. The mixture is heated nearly to boiling for ten minutes, then boiled, the precipitated arsenic collected on a filter, washed with hot dilute hydrochloric acid, then with water, and its quantity estimated by titration with iodine solution. In samples containing a small quantity of arsenic a relatively large weight of the sample may be taken for the estimation, and the greater part of the lead separated as sulphate before the arsenic is precipitated by hypophosphorous acid.

*Manganese-gold alloys.* N. Parravano. Gaz. Chim. Ital., 1915, 45, 1, 293—303.

THE curve representing the solidifying points of manganese-gold alloys falls from  $1084^\circ\text{C}$ ., the melting point of gold, to  $990^\circ\text{C}$ . at 10.5% Mn, then rises to  $1225^\circ\text{C}$ . at 21.8% Mn, falls to  $1080^\circ\text{C}$ . at 46% Mn, and then rises to  $1247^\circ\text{C}$ ., the melting point of manganese, with a horizontal portion at 50—57.5% Mn, corresponding to a region of partial miscibility in the liquid state. With up to 10.5% Mn the alloys consist of solid solutions; from 10—14% there is an eutectic in addition to the primary crystals. The maximum at  $1225^\circ\text{C}$ . corresponds to the compound AuMn. Alloys with 14—30% Mn are composed of a single constituent—either AuMn or a solid solution; from 30 to 46% Mn there is an eutectic in addition to the primary crystals. The saturated solid solution at the manganese end of the series contains about 25% Au. The compound AuMn is represented by a minimum on the curve showing the hardness of alloys containing up to 35% Mn.—A.S.

*Alloys of mercury with thallium.* P. Pavlovitch. J. Russ. Phys. Chem. Soc., 1915, 47, 29—46. J. Chem. Soc., 1915, 103, ii, 262—263.

THE author has investigated the complete melting-point diagram of the system Hg—Tl, the electrical conductivity of the alloys containing 0—40% Tl, and the hardness, by Brinell's method, of the alloys containing 90—100% Tl. The existence in the fusion diagram of an irrational maximum, not corresponding with simple atomic proportions of the constituent atoms, is confirmed; the composition at this maximum is 29—30 atoms % Tl. The curve of conductivity shows a maximum at 26—28 atoms % Tl, and the potential curve a re-entrant angle at 27—28.4 atoms % Tl, both of these being also irrational points. This irrationality may be explained by the existence of the dissociating compound,  $\text{Hg}_2\text{Tl}$ , which forms with the components solid solutions within the limits 21—31 atoms % Tl. According to Stepanov's rule, the magnitude of the temperature-coefficient of resistance, which approximates to that for pure metals (0.004), indicates the existence of a chemical compound in the  $\alpha$ -phase. Within the limits 86—100% Tl, the latter forms with mercury  $\beta$ -solid solutions, characterised by enormously increased hardness.

*Palladium and hydrogen.* II. A. Sieverts. Z. physik. Chem., 1914, 85, 451—478. J. Chem. Soc., 1915, 103, ii, 268—269. (Compare this J., 1914, 751.)

THE relationship between the quantity of hydrogen

absorbed and the partial pressure was investigated between 138° and 821° C. and at hydrogen pressures between 1 and 760 mm., using the same palladium and the same apparatus as previously employed. With both commercial and pure palladium wire, between the temperature limits mentioned, the quantity of hydrogen absorbed,  $L_p$ , by unit weight of palladium is not strictly proportional to the square root of the hydrogen pressure  $p$ . The experimental results are better expressed by the equation,  $L_p = k_1 p^{1/2} + k_2 p$ , in which  $k_1$  and  $k_2$  are constants depending on the temperature; the equation is not true for higher pressures. This expression can be regarded as representing that the hydrogen molecules are in equilibrium with hydrogen atoms, both in solution in the palladium and in the gas phase, and that Henry's law holds strictly for both atoms and molecules. The dissociation constant of hydrogen is 25 at 138°; 109 at 315°; 112 at 619°; and 102 at 821° C. The quantity of hydrogen absorbed by unit weight of palladium depends only on the pressure and temperature, and is entirely independent of the surface area of the metal; consequently, the absorption of hydrogen by palladium is to be regarded as a true solution phenomenon. The isothermals of palladium-black and palladium-sponge are similar to those of compact palladium, but the actual curves are different with different specimens, and are apparently dependent on the nature of the palladium. The similarity of the absorption isothermals in all cases indicates that in palladium-black and palladium-sponge the absorption is mainly due to solution of the hydrogen, at least at temperatures above 100° C. At lower temperatures it is, however, likely that surface adsorption accounts for a large portion of the hydrogen taken up. The above results are in strict accord with the statement (*loc. cit.*) that palladium-black and palladium-sponge are made up of varying quantities of amorphous and crystalline palladium. Both modifications appear to act as solvents for hydrogen with different powers of solution.

**Metals; The passage of electricity through** — J. J. Thomson. *Inst. of Metals*, May, 1915. *Engineering*, 1915, 99, 577—579.

The limitations of the "free-electron" theory of conduction are considered, and an analogy is established between the passage of an electric current through a metallic conductor under an applied electromotive force and the "flow" of magnetism through a bar of soft iron under a magnetomotive force. According to this hypothesis, all bodies are built up of "dipoles" analogous to the elementary magnets of the iron bar, each consisting of a positive and a negative charge separated by a small distance; the function of the electric force is to cause the dipoles to point in one direction and thus form chains of doublets, the maintenance of which depends on the intensity of the intermolecular collisions or thermal agitations occurring in the material. The dipoles of metals part with electricity much more easily than those of other materials, the pull of adjacent dipoles on each other being resisted in the case of non-conductors, but resulting in the passage of a definite number of electrons per second through any given metal. On this theory the phenomena of dielectric polarisation (Maxwell's displacement current) and the super-conductivity of pure metals at low temperatures (4° C. absolute, obtained by means of liquid helium), observed by Onnes, are satisfactorily explained.—W. E. F. P.

#### PATENTS.

**Iron; Process and furnace for obtaining metallic from friable ores.** Eisenwerk Jagstfeld Ges. m. b. H. Ger. Pat. 282,574, March 13, 1913.

The ore is reduced to spongy iron by carbon

monoxide in a rotary kiln, sintering being avoided, and the reduced iron is transferred to a low shaft furnace, where it is melted with the aid of low-grade fuel and an air blast of low pressure. Part of the carbon monoxide produced by combustion of the fuel is used in the first stage of the process.—A. S.

**Iron and steel alloys containing tantalum; Manufacture of** — Siemens und Halske A.-G. Ger. Pat. 282,575, March 4, 1913.

TANTALUM is added to the iron or steel in the form of a nickel-tantalum alloy. An alloy of 80 parts of iron or steel with 10 of nickel and 10 of tantalum, for example, possesses great strength, elasticity, and hardness.—A. S.

**Furnaces; Metal melting** — I. Hall, Birmingham. Eng. Pat. 3035, Feb. 25, 1915. Addition to Eng. Pat. 5664, March 6, 1914 (this J., 1914, 869).

THE valve of the melting pot is actuated and controlled by means of a vertical hand-screw engaging with one extremity of the pivoted lever.—W. E. F. P.

**Furnace; Ore-smelting** — G. P. Gibson, Braddock, Pa. U.S. Pat. 1,138,651, May 11, 1915. Date of appl., Aug. 6, 1914.

THE apparatus consists of two groups of vertical blast-furnace units arranged, one on either side, above a closed, horizontal melting furnace into which they discharge; the hearth of the latter slopes downwards from the sides to a central metal pit. Each furnace is heated independently.—W. E. F. P.

**Crucible-furnace.** E. Hallgren, Bellevue, Pa. U.S. Pat. 1,138,866, May 11, 1915. Date of appl., Nov. 14, 1914.

THE melting chamber has an open lower end, stationary side-walls, and a solid roof. The lower end may be closed by a bottom which can be moved vertically by a plunger. Means are also provided for moving the bottom horizontally below the melting chamber out of the path of the vertical movement.—T. St.

**Zinc furnaces; Briquettes for use in** — G. S. Brooks, Depue, Ill. Assignor to The New Jersey Zinc Co., New York. U.S. Pat. 1,137,835, May 4, 1915. Date of appl., Nov. 28, 1913.

THE briquettes are composed of 4 parts of ore and 1—1½ parts of coal of the usual fineness, together with 1 part of more finely powdered material, e.g., ore, coal, or zinc oxide. The mixture is formed into a plastic mass with salt solution, briquetted, and slowly dried so as to bring the salt towards the surface, where it forms a protective coating. The briquettes may be made to conform in cross-section to the interior of the retort.—W. R. S.

**Ores; Process of leaching** — J. A. McCaskell, Salt Lake City, Utah. U.S. Pat. 1,137,874, May 4, 1915. Date of appl., June 2, 1914.

CHLORINE gas is produced electrolytically from saturated sodium chloride solution in a cell, the anode compartment of which is separated from the cathode compartment by a layer of mercury, which absorbs the sodium. The ore is agitated with the chlorine under pressure, and the filtered liquor is then electrolysed in the cathode compartment, the dissolved metal being deposited and sodium chloride regenerated in contact with the mercury.—W. R. S.

*Wires, bands, etc.; Process of producing and protecting insulating coverings of oxide on—*. E. W. Küttner, Berlin. U.S. Pat. 1,137,986, May 4, 1915. Date of appl., Sept. 2, 1910.

THE surfaces of coils of wire containing aluminium are oxidised and simultaneously treated with a solution which, after the evaporation of the solvent, will yield a mechanically strong coating on the wires, thereby protecting the oxidised surfaces against damage by pressure. The solution is introduced into the interior of the coil and between the individual turns, the coil being subsequently heated an optional number of times.—T. St.

*Case-hardening compound*. A. O. Blaich, Chicago, Ill. U.S. Pat. 1,138,073, May 4, 1915. Date of appl., Oct. 18, 1913.

THE compound consists of charred leather impregnated with a small percentage of a sodium salt and of calcium carbonate.—T. St.

*Metallurgical apparatus*. H. B. Faber, Brooklyn, N.Y. U.S. Pat. 1,138,284, May 4, 1915. Date of appl., Jan. 10, 1905.

PARTS of metallurgical apparatus are formed of such dissimilar metals (hard lead, bronze, etc.) as are capable of resisting corrosion in the presence of a dissociating solvent, and an "iron-glass insulator" is interposed between the parts so as largely to prevent galvanic action.—W. E. F. P.

*Metallic compound [alloy]*. H. B. Coho, Mount Vernon, N.Y. U.S. Pat. 1,138,845, May 11, 1915. Date of appl., Sept. 22, 1914.

AN alloy of lead and copper containing "needles antimony" (antimony sulphide).—W. E. F. P.

*Metals; Recovering—by electrolysis*. L. Addicks, Douglas, Ariz. U.S. Pat. 1,138,921, May 11, 1915. Date of appl., Nov. 5, 1914.

METALS, such as copper, are reduced electrolytically in the presence of a depolariser having a solvent action upon the metal, the action being carried out in the presence of a salt, such as aluminium sulphate, which will counteract the solvent action. The salt is present in amount sufficient to reduce materially the action on the cathode, and yet insufficient to deaden its effect.—B. N.

*Amalgamator*. C. W. Patten, Lynn, Mass. U.S. Pat. 1,139,007, May 11, 1915. Date of appl., Jan. 17, 1914.

A RECEPTACLE of larger diameter at the top than at the bottom contains mercury in its lower portion. Above the mercury is a central vertical shaft carrying a screw-propeller with inclined horizontal blades, the lowest of which are just above the surface of the mercury, and the upper above the overflow edge of the receptacle. A mixture of ore and water is forced through the mercury from below its surface, the ore being elevated and discharged at the overflow edge by the rotation of the propeller.—W. R. S.

*Gold-separating mechanism*. F. W. Stevens, Newton, Mass., Assignor to A. Hopewell, Wellesley, Mass. U.S. Pat. 1,139,143, May 11, 1915. Date of appl., Jan. 23, 1914.

MERCURY is contained in a receptacle having a bottom sloping downwards towards the centre, and gold-bearing gravel is fed in by means of a screw conveyor through a feed pipe passing up through the centre of the bottom to just above the surface of the mercury. A rotary disc, with inwardly inclined feeding surface partially submerged in the mercury, discharges the gravel at the periphery.—W. R. S.

*Amalgamator*. F. P. Arnold, Carbondale, Pa., and G. F. Wedeman, Washington, D.C. U.S. Pat. 1,139,324, May 11, 1915. Date of appl., May 23, 1914.

THE amalgamator consists of a receptacle having a narrow open top with means for feed and discharge on opposite sides, and provided with several endless chains, placed vertically, which travel in a direction opposite to the flow of pulp, and act as agitators. The wall of the receptacle on the feed side is parallel to one flight of the agitators, whilst the discharge side is inclined to the other. A vertical partition depending from the centre extends across the vessel, and is shallower than the agitators. The lower part of the receptacle serves as a mercury chamber.—H. R. D.

*Ore-separator*. H. H. McGovern, Oak Grove, Oreg. U.S. Pat. 1,139,206, May 11, 1915. Date of appl., July 8, 1914.

IN a centrifugal apparatus consisting of two nested bowls, spaced apart and adapted to rotate together about a vertical axis, the inner bowl is open at the bottom and is provided with a central, vertical funnel through which ore-pulp is fed into the lower part; the rims of the bowls have overlying flanges between which means are provided for adjusting the spacing. The pulp is thus divided into two portions, each of which is concentrated and discharged separately.—W. E. F. P.

*Ores; Apparatus for treating—*. B. MacDonald, South Pasadena, Cal. U.S. Pat. 1,139,428, May 11, 1915. Date of appl., May 6, 1914.

A TANK in which ore is treated with solution is provided with a perforated conical false bottom, forming with the real bottom a receptacle into which the solution flows after percolating through the ore. Means are provided for forcing the solution from this receptacle up a vertical pipe to be discharged again over the ore in the tank. The receptacle is also provided with a pipe for running the solution into a precipitation tank, and with a pipe communicating with a gas chamber. At the base of the false bottom is a shoot for the removal of treated ore.—T. St.

*Fusible material [metal]; Coating with—*. C. F. Jenkins, Washington, D.C. U.S. Pat. 1,139,291, May 11, 1915. Date of appl., Dec. 16, 1914.

SMALL quantities of the fusible metal are melted successively by the passage of an electric current, and each small quantity is projected violently against the article to be coated by successive actions of highly explosive agents. The expansion due to the partial volatilisation of the metal also has a propulsive and disintegrating action on the molten metal.—T. St.

*Tin scrap; Apparatus for detinning—*. H. Goldschmidt, Essen, Germany, Assignor to Goldschmidt Detinning Co., New York. U.S. Pat. 1,139,410, May 11, 1915. Date of appl., Dec. 24, 1906.

AN alkaline electrolytic bath is provided with electrodes movable in a circuit into, and out of, the bath. The anodes carry baskets containing the articles to be detinned. The cathodes on leaving the bath are stripped of the spongy tin deposit, and the latter is collected and compressed by insulated rollers.—W. R. S.

*Tin; Furnace for the recovery of— from sweepings or residues*. Gebr. Karges. Ger. Pat. 280,465, Feb. 28, 1914.

THE roof of the fire-chamber slopes downwards on both sides from the middle and forms the floor of the removable melting chamber above. The

melting enamel is surrounded by an outer casing, and the fire-gases pass upwards through the intermediate space and also through a vertical pipe in the centre of the melting chamber. The tin melts and is tapped off through openings at the bottom.  
—A. S.

*Zinc, cobalt, and other constituents from the waste liquors obtained in the extraction of copper; Electrolytic recovery of* — J. P. A. Larson and G. K. L. Helme. Ger. Pat. 280,525, Nov. 24, 1912.

ZINC is recovered electrolytically from the waste liquor, and a suitable agent, e.g., a metal, metallic oxide or hydroxide, or a salt capable of being converted into a higher stage of oxidation, is added to prevent the liberation of free acid or chlorine during electrolysis. When electrolysis is complete the solution is diluted to precipitate iron compounds and render it suitable for discharge into streams. The deposited zinc contains some iron, copper, and cobalt, and in the subsequent refining the copper and cobalt are recovered.—A. S.

*Bearing metal; Production of a* — by spraying W. A. Guertler. Ger. Pat. 280,752, June 18, 1913.

A BEARING metal composed of a soft ground mass of which the chief constituent is lead, with particles of a hard material consisting essentially of iron embedded therein, is produced by spraying the components in the liquid state or in the form of very fine powder, and if necessary with simultaneous or subsequent thermal or mechanical treatment of the product. The lead may be mixed or alloyed with small quantities of zinc, aluminium, tin, antimony, bismuth, phosphorus, or silicon, and the iron may be alloyed with small quantities of nickel, copper, cobalt, manganese, chromium, tungsten, molybdenum, vanadium, titanium, silicon, or carbon.—A. S.

*Nickel alloys of high chemical resistance and which can be worked mechanically.* W. and R. Borchers. Ger. Pat. 281,784, May 30, 1914. Addition to Ger. Pat. 278,903.

IN order to increase the resistance to high temperatures of the alloys described in the chief patent (this J., 1915, 235), the proportion of gold, or, preferably, of a metal of the platinum group, is increased, e.g., up to 40%.—A. S.

*Ores and solid salts; Treatment of* — by electrochemical reduction. A. A. M. Hanriot, Paris. Eng. Pat. 11,950, May 14, 1914. Under Int. Conv., May 22, 1913.

SEE Fr. Pat. 480,516 of 1913; this J., 1915, 36.

*Zinc and other metallic vapours; Condensation of* — C. V. and J. M. J. Thierry, Paris. Eng. Pat. 13,702, June 5, 1914.

SEE Fr. Pat. 472,879 of 1914; this J., 1915, 558.

*Aluminium and aluminium alloys; Compound for welding* — E. Thaulow, Frederiksberg, Denmark. U.S. Pat. 1,139,923, May 18, 1915. Date of appl. March 4, 1914.

SEE Eng. Pat. 5356 of 1914; this J., 1915, 286.

*Bismuth; Process for separating* — from copper. W. Thum, Hammond, Ind., U.S.A. Eng. Pat. 12,135, May 10, 1914.

SEE U.S. Pat. 1,098,854 of 1914; this J., 1914, 704.

*Boiler for utilising waste heat [from regenerative metallurgical furnaces].* U.S. Pat. 1,138,346. See 1.

*Gas producers, blast-furnaces, or the like.* Eng. Pat. 18,381. See 11A.

*Method of treating water [and utilising slag].* U.S. Pat. 1,139,618. See XIXn.

## XI.—ELECTRO-CHEMISTRY.

*Electrochemical reactions caused by passage of a current across the boundary of a gas into an electrolyte.* F. Haber and A. Klemenc. Z. Elektrochem., 1914, 20, 485—488. J. Chem. Soc., 1915, 108, ii., 212—213.

TO determine the rôle of the electrode in the oxidation or reduction of depolarisers, sulphuric acid of various strengths was electrolysed in a vessel so constructed that it could be exhausted, and one electrode could be fixed a few mm. above the liquid. Experiments were carried out at a series of temperatures, using in all cases a voltage of 600. When the cathode was in the gas more hydrogen was obtained than the Faraday law demands, whilst persulphuric acid and Caro's acid were formed in the solution. The formation of these substances and of hydrogen peroxide was more noticeable when the anode was in the gas. The concentration of active oxygen (Caro's acid, persulphuric acid, and hydrogen peroxide) increases with increasing concentration of the sulphuric acid up to 45%, when it begins to fall off, and at 75% sulphuric acid there is no formation of these substances. A considerable cooling diminishes the amount of these substances, although the amount produced is still in excess of that demanded by Faraday's law. If oxygen is led into the anode chamber up to a pressure of 131 mm. there is also a decrease in the amount of active oxygen. Increase in the length of time or in the current strength has no marked effect. The results lead to the view that at the electrode a strongly oxidising product is formed from the water. This is taken up by the solution, and is sufficiently stable to oxidise the sulphuric acid, forming persulphuric acid, Caro's acid, and hydrogen peroxide.

*Leclanché cells; Depolarisation in* — M. de K. Thompson and E. C. Crocker. Amer. Electrochem. Soc., April, 1915. Met. and Chem. Eng., 1915, 13, 319.

THE greatest depolarising efficiency of mixtures of manganese dioxide and carbon was attained with 55—60% of pyrolusite and with particles of uniform size (0.03—0.1 sq. in. aperture). Depolarisation due to hydrogen was entirely prevented by the manganese dioxide; that due to ammonia was largely overcome by the addition of zinc chloride to the solution.—W. R. S.

*Relationship between electrolytic and pure chemical processes. [Action of a mixture of sulphuric acid and hydrogen peroxide on metals.]* Reichenstein. See X.

### PATENTS.

*Storage battery. Electrolyte.* R. Hurley, Assignor to J. C. Farr, jun., Hoboken, N.J. U.S. Pats. (A) 1,138,226 and (B) 1,138,221, May 4, 1915. Dates of appl., Dec. 28, 1912.

(A) THE battery is composed of two copper shells, the inner surface of the outer one being coated with zinc amalgam, so that it acts as a negative electrode. The outer and inner surfaces of the inner shell are coated with mercury and zinc amalgam respectively, thus forming positive and negative electrodes. A lead plate in the inner shell acts as a positive electrode. (B) A mixture of lead and zinc sulphates, sulphuric acid, and water.—B. N.

*Negative-pole plate for alkaline storage batteries. Electrolyte for secondary batteries.* W. Morrison, Des Moines, Iowa. U.S. Pats. (A) 1,139,213 and (B) 1,139,214, May 11, 1915. Dates of appl., Aug. 6, 1913, and Sept. 11, 1914.

(A) AN insoluble zinc-titanium compound, obtained by mixing solutions of a zinc salt and a

soluble titanate, is mixed with a mercury compound and applied as a paste to an electrode support. The mixture is reduced electrolytically in an alkaline electrolyte. (b) Titanic acid is dissolved in sulphuric acid.—B. N.

*Electrolytic cell; Method of operating an* — [for the production of chlorine]. E. E. Werner, Indianapolis, Ind. U.S. Pat. 1,139,389, May 11, 1915. Date of appl., Aug. 3, 1914.

CHLORINE is generated electrolytically from a salt solution, by continuously introducing into the cathode chamber, at the surface of the electrolyte, a specifically lighter liquid, which dissolves the solid waste products formed in the chamber. The liquid containing the dissolved products is discharged continuously from the chamber at a point above the normal surface of the electrolyte.—B. N.

*Insulating material.* W. J. Longmore, Bellevue, Pa., Assignor to Westinghouse Electric and Manufacturing Co. U.S. Pat. 1,138,676, May 11, 1915. Date of appl., Feb. 16, 1912.

A SHOWER of mixed mica flakes and finely powdered, dry binding material is distributed upon a heated plate within a chamber, heat and pressure being applied subsequently to the upper surface of the material in the chamber, so as to compress it into an insulating sheet. The process is then repeated, heated plates being used to separate the successive layers of material.—B. N.

*Mica insulation; Producing* — J. R. Sanborn, Pittsburgh, Pa., Assignor to Westinghouse Electric and Manufacturing Co., Pa. U.S. Pat. 1,138,691, May 11, 1915. Date of appl., Aug. 10, 1910.

Mica flakes and powdered insulating binding material, in suitable quantities, are projected into the upper portion of a chamber, which is restricted laterally but elongated vertically, and the deposited mass is heated and compressed to convert it into a sheet.—B. N.

*Carbon articles [electrodes, etc.]; Manufacture of* — Gebr. Siemens und Co. Ger. Pat. 282,106, Feb. 11, 1914.

COLLOIDAL graphitic acid is used as binding medium for the carbon, and the shaped object is heated to a temperature at which the graphitic acid decomposes, with separation of carbon.—A. S.

*Apparatus for electrolysis of alkali chlorides.* U.S. Pat. 1,138,400. See VII.

*Electrochemical process of treating waters, liquids, and sewage.* U.S. Pat. 1,139,778. See XIXb.

*Water-purifying apparatus.* U.S. Pat. 1,139,969 and 1,139,970. See XIXb.

## XII.—FATS; OILS; WAXES.

*Fats; Preparation of optically active* — II. Synthesis of optically active monobromohydrin, epihydrin alcohol, aminopropanediol, and propionin. E. Abderhalden and E. Eichwald. Ber., 1914, 47, 2880—2888. J. Chem. Soc., 1915, 108, i, 210—211.

THE optically active epibromohydrins (see this J., 1914, 700) were converted into the corresponding monobromohydrins by the action of formic acid and saponification of the resulting formyl-monobromohydrins. Elimination of hydrogen bromide from the monobromohydrins gave rise to the corresponding epihydrin-alcohols, and

these yielded the corresponding aminopropanediols,  $\text{NH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ , by the action of aqueous ammonia. By the prolonged action of propionic acid on *d*-epihydrin-alcohol, a dextro-rotatory ester, mono- or di-propionin, was obtained, which is the first synthetic, optically active fat.

*Palm-kernel oil.* A. Heiduschka and A. Burger. Z. offentl. Chem., 1914, 20, 361—369. Z. angew. Chem., 1915, 28, Ref., 97—98.

THE following average values are given for palm-kernel oil:—Saponif. value, 253.4; Reichert-Meissl value, 6.8; Polenske value, 9.4; iodine value (Hühl), 15.02; mean molec. weight of non-volatile fatty acids, 228.2. The non-volatile fatty acids consisted of 17.75% oleic acid, 23.27% myristic acid, and 58.98% lauric acid. The total volatile acids, soluble and insoluble (5.20%), contained capric, caprylic, and caproic acids. No stearic, palmitic, linolic, or linolenic acid was found. Fachini and Porta's method of separating insoluble fatty acids, by treatment of their potassium salts with acetone, is useful as a qualitative test, whilst Heintz's method of fractional precipitation with magnesium acetate gives good results when the quantity of fatty acid is not less than 0.05 gm. —C. A. M.

*Fats; Constituents of animal* — Fat of *Equus caballus* [horse fat]. J. Klimont, E. Meisl, and K. Mayer. Monats. Chem., 1914, 35, 1115—1127. Z. angew. Chem., 1915, 28, Ref., 187—188.

FOUR commercial samples of horse fat of about the same consistence were purified and then gave the following values:—Iodine value, 74.9—78.1; acid value, 1.40—2.91; saponification value (3 samples), 193.1—200.4. The sp. gr. was 0.9373 and 0.9461 at 15°C. for two samples and 0.9148 and 0.9184 at 27°C. respectively for the others; the m. pts. were 20°—41°C., 22°—38°C., 29.5°C., and 33°C. respectively; the fatty acids from two samples melted in both cases at 37°—39°C. In the liquid portion of the fat oleic, linolic, and linolenic acids were detected. The solid portion when crystallised repeatedly from acetone to which one-twentieth of its volume of chloroform was added, yielded a glyceride of m. pt. 60°C. and saponification value 197. The fatty acid separated from this glyceride was identified as heptadecylic acid (margaric acid), m. pt. 57°—57.5°C., neutralisation value, 208. The fatty acid from goose fat, described as an eutectic mixture of stearic and palmitic acids, also actually consists of heptadecylic acid.—A. S.

*Prunus domestica; The oil and amygdalin content of the seed kernels of* — G. Kassner and K. Eckelmann. Arch. Pharm., 1914, 252, 402. Chem.-Zeit., 1915, 39, Rep., 162.

PLUM-STONE kernels from trees grown on well manured soil yielded 42.92% of a pale yellow, fatty oil of mild taste similar to almond oil, having sp. gr. at 15°C., 0.916, acid value 1.44, saponification value 188.1, ester value 186.66; iodine value 104. The kernels contained 1.82% of amygdalin. —T. C.

*Strophanthus seeds; Oil of* — H. Matthes and L. Rath. Arch. Pharm., 1914, 252, 683—693. Z. angew. Chem., 1915, 28, Ref., 163.

THE oil from *Strophanthus Kombé* seeds contains 21% of solid saturated and 73% of unsaturated fatty acids. The saturated acids contain 30% of stearic acid and 70% of palmitic acid. The liquid fatty acids are a mixture of 80% of oleic acid and 20% of linolic acid. *Strophanthus* seed oil only contains one phytosterol, sitosterol (m. pt. 137°; acetate, m. pt. 127°—128°C.), and does not contain arachidic acid.—F. W. A.

*Strophanthus seed oil; Unsaponifiable constituents of* —. A. Heiduschka and R. Wallcreuter. Arch. Pharm., 1914, 252, 704—708. Z. angew. Chem., 1915, 28, Ref., 163.

STROPHANTHUS seed oil contains 1.12% of unsaponifiable constituents of which 0.504% is sitosterol. (See also preceding abstract.)—F. W. A.

*Dihydroxy- and tetrahydroxy-stearic acid; Separation of* —. H. Matthes and L. Rath. Arch. Pharm., 1914, 252, 699—703. Z. angew. Chem., 1915, 28, Ref., 163.

By the oxidation of the liquid fatty acids of Strophanthus seed oil with potassium permanganate, 20% of tetrahydroxy- and 80% of dihydroxy-stearic acid were obtained, separation being effected with ether in a Soxhlet apparatus. —F. W. A.

*Oils; Action of chlorine on* —. L. Meunier and L. Wierchowski. Collegium, 1914, 610. Z. angew. Chem., 1915, 28, Ref., 98—99.

CHLORINE acts upon oils, forming at 90° C. both substitution and addition compounds. After 9 hours' chlorination a sample of cod liver oil had increased in sp. gr. from 0.9258 to 0.9950; in viscosity at 50° C. from 3.12 to 7.46; had absorbed 12.80% Cl, and contained 6.95% oxidised fatty acids. The emulsifying properties of the oil increased with the degree of chlorination. At the ordinary temperature the chlorinated oil lost only a trace of hydrochloric acid in 3 days. When boiled for three hours with water, 0.72% of the chlorine was replaced by hydroxyl groups. Linseed oil gave the following results when treated with chlorine:—

Duration, hours.	Sp. gr.	Viscosity at 50° C.	Chlorine, %	Increase in weight, %
0	0.9325	2.90	0	0
9	0.9722	4.86	6.88	7.7
19	1.0137	8.09	12.23	14.36

—C. A. M.

*Phytosterol in animal fats; Detection of* — by precipitation with digitonin. B. Kühn and J. Wewerinke. Z. Unters. Nahr. Genussm., 1914, 28, 369—379. Z. angew. Chem., 1915, 28, Ref., 11.

SEPARATION of the phytosterol and cholesterol by precipitation with digitonin yields more satisfactory results than are obtained by Bömer's method, but the precipitation should be made from the fatty acids and not directly from the glycerides. (See also this J., 1914, 651.)—W. P. S.

*Palmitates; Physico-chemical studies of solutions of* —. K. Arndt and P. Schiff. Kolloid-Chem. Beihefte, 1914, 6, 201—230. J. Chem. Soc., 1915, 103, ii., 237.

THE authors investigated the electrical conductivity and the viscosity of N/10 and N/100 solutions of sodium and potassium palmitate between 25° and 85° C. Observations were also made in order to elucidate the nature of the coagulation process. The coagulated soap consists of a mixture of acid and normal palmitate, the composition of the mixture varying with the concentration of the solution. Coagulation consists in the reversible transformation of the sol into the gel form, but equilibrium is only attained very slowly. The coagulation temperature depends, not only on the concentration of the solution, but also on the nature of the cation. For the sodium salt, the temperatures are about 30° C. higher than for equally concentrated solutions of the potassium salt. Differences are also found

in the effect produced by the addition of the corresponding chlorides, in that the addition of an equivalent quantity of sodium chloride to N/10 sodium palmitate solution raises the coagulation temperature by 7° C., whilst the addition of potassium chloride to a solution of potassium palmitate has no appreciable effect.

*Composition and effects of lupin seeds [due to enzymes]. [Detection of lupin seeds in admixture with castor oil seeds.]* Muenk. See XVIII.

*Value of sludge from town sewage as a source of fat.* Holde. See XIX.

#### PATENTS.

*Unsaturated organic [fatty] material; Hydrogenating* —. C. Ellis, Montclair, N.J. U.S. Pat. 1,133,201, May 4, 1915. Date of appl., April 24, 1912.

THE fat, etc., is mixed with nickel carbonyl and hydrogen and heated to decompose the carbonyl and cause the nickel and hydrogen to act upon the fat, the hydrogenation being then completed at a lower temperature.—C. A. M.

*Alkali-free detergent for scouring and dyeing.* U.S. Pat. 1,139,826. See VI.

*Process of obtaining a substitute for linseed oil or varnish.* Ger. Pat. 282,308. See XIII.

#### XIII.—PAINTS; PIGMENTS; VARNISHES; RESINS.

*Red lead specifications.* Oil, Paint, and Drug Rep., May 17, 1915.

THE U.S. Navy Department issued on April 1, 1915, specification No. 5212a, for red lead, as follows:—Red lead, dry, shall contain not less than 94% of true red lead (Pb<sub>3</sub>O<sub>4</sub>), the remainder to be practically pure lead monoxide (PbO). It shall not contain more than 0.1% of metallic lead, 0.1% of alkali as Na<sub>2</sub>O, and 0.05% of total impurities which include all substances other than lead oxides. It must be of such fineness that not more than 0.5% remains after washing with water through a No. 21 silk bolting cloth sieve. It shall be of good bright colour and equal to the standard sample in freedom from vitrified particles and in other respects. When mixed with pure linseed oil, petroleum spirit, and drier, as per standard formula, viz.: Red lead, dry, 20 lb.; raw linseed oil, 5 pints; petroleum spirit, 2 gills; drier, 2 gills, and applied to a smooth, vertical iron surface, it must dry hard and elastic without running, streaking, or sagging.

*Linseed oil varnish; Approximate determination of non-volatile unsaponifiable substances in* —. F. Barany. Z. anal. Chem., 1914, 53, 634—635. J. Chem. Soc., 1915, 108, ii., 293.

THE presence of appreciable quantities of mineral oil or rosin oil may be detected and the amount estimated by boiling 10 grms. of the varnish for 20 mins. with 30 c.c. of alcohol and 5 c.c. of aqueous 50% potassium hydroxide solution. The solution is then diluted with alcohol to 50 c.c., shaken with 100 c.c. of light petroleum, and, after addition of 100 c.c. of water, again shaken gently; 50 c.c. of the light petroleum layer is withdrawn, evaporated, and the residue dried at 100° C. and weighed.

*Mangostin; a crystalline substance allied to the resins.* J. R. Hill. Chem. Soc. Trans., 1915, 107, 595—601.

THE dried skins of the fruit of the mangosteen tree

*Garcinia mangostana*) contain about 10% of a resin of which about half consists of mangostin,  $C_{22}H_{34}O_6$ , a colourless, tasteless substance crystallising in small, flat, pale yellow needles, m. pt. 181°—182° C., possessing many of the physical characteristics of the resins. Mangostin is insoluble in water and in alkali carbonates but readily soluble in most organic solvents and in alkali hydroxides. It contains two phenolic groups, one methoxy group, and one or more amyl groups, and on methylation with methyl sulphate and dilute caustic potash solution yields dimethylmangostin, m. pt. 123° C., crystallising in long silky needles. Mangostin is converted by hydriodic acid into a monohydroxy compound, m. pt. 180°—181° C., giving a methyl and an acetyl derivative of m. pt. 216° and 218°—219° C. respectively. Mangostin in alcoholic solution gives a greenish-brown coloration with ferric chloride. Oxidation with nitric acid or potassium permanganate solution converts it largely into oxalic acid.—T. C.

## PATENTS.

*Oil paints; Preparation of*.—W. J. Randall, Bristol. Eng. Pat. 1441, Jan. 29, 1915.

A solution of a solid mineral hydrocarbon, such as those of the paraffin or olefine series, with or without a solution of a vegetable wax, is added to the usual ingredients of oil paints. The following are two examples of such paint compositions drying with a "flat" and a glossy finish respectively:—(1) Zinc oxide or sulphide, 320 lb.; barium sulphate, 40 lb.; china clay, 40 lb.; and 200 lb. of the following mixture:—a solution prepared by dissolving 1 lb. solid mineral hydrocarbon, with or without 1½ oz. of vegetable wax, in 1 gallon of oil of turpentine at 130°—140° F. (54°—60° C.); copal varnish, 1 gall.; oil of turpentine, 1 gall.; Dutch "stand" oil, ½ gall.; driers, ½ gall.; ground calcined borax, 2 oz. (2) Red oxide powder, 400 lb.; boiled linseed oil, 100 lb.; and 150 lb. of a mixture of 1 lb. solid mineral hydrocarbon, with or without 1½ oz. of vegetable wax, dissolved in ½ gallon of oil of turpentine at 130°—140° F. (54°—60° C.); copal varnish, 1 gall.; boiled linseed oil, 2½ galls.; and driers, ½ gall.—E. W. L.

*White pigment [lithopone]; Inalterable—and process of making same*. R. B. Llopert, Cordoba, Argentina. U.S. Pat. 1,139,427, May 11, 1915. Date of appl., Feb. 19, 1915.

AQUEOUS solutions of pure zinc sulphate and barium sulphide are mixed, and the precipitate is dried and calcined out of contact with air at about 500°—700° C. The calcined product is cooled rapidly by immersing in water and changing the water until the lithopone is cold, when it is ground, washed in water, heated to about 80°—100° C., pressed, and rapidly dried below 100° C.—T. ST.

*Unsaturated hydrocarbons; Production of new compounds of—and of solutions and compositions containing the same*. F. E. Matthews and H. M. Elder, London. Eng. Pat. 11,635, May 11, 1914.

COMPOUNDS of sulphur dioxide with unsaturated hydrocarbons are produced by direct combination. This may be effected, for instance, by exposing the mixed liquids to sunlight or ultra-violet light, or in some cases by heating. The examples given are the compounds with pseudo-butylene ( $C_4H_8SO_2$ ), propylene, amylene, and ethylene. The butylene product is a horny or glassy, clear white solid, soluble in chloroform or tetrachloroethane, and not easily inflammable. It can be used for making varnishes, transparent films, etc., and may be mixed with celluloid by first softening both with acetone; it renders the celluloid less inflammable.—B. V. S.

*Linseed oil or varnish; Process of obtaining a substitute for*.—E. F. Waentig. Ger. Pat. 282,306, June 1, 1912. Addition to Ger. Pat. 272,465.

IN the preparation of a substitute for linseed oil or varnish from animal or fish oils according to the process described in the chief patent (this J., 1914, 604), distillation is effected *in vacuo* at 270°—285° C., and unsaturated fatty acids or resin acids or their esters are added to the contents of the still when the greater part of the saturated acids has been removed. The treatment with highly superheated steam is stopped before the saturated fatty acids have been completely removed, and distillation is completed with steam at 315° C.—A. S.

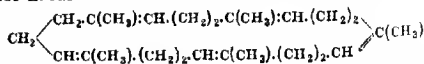
*Production of colour lakes from vegetable substances containing the dyestuff as glucoside*. Ger. Pat. 281,423. See IV.

*Process for coating porous substances [wood]*. U.S. Pat. 1,139,470. See IX.

## XIV.—INDIA-RUBBER; GUTTA-PERCHA.

*Caoutchouc and allied compounds; Constitution of*.—C. Harries and E. Fonrobert. *Annalen*, 1914, 406, 173—226. J. Chem. Soc., 1915, 108, i., 277—279.

PARA caoutchouc was converted into its hydrochloride and the latter heated with anhydrous pyridine at 125°—145° C. The regenerate I. thus obtained had the same composition as, but was not identical with, the original caoutchouc. By ozonisation in ethyl acetate solution, it yielded an ozonide, by the decomposition of which by water at about 125° C. the following substances were produced, the percentage being given in brackets: oxygen (0.068), hydrogen (0.044), carbon monoxide (0.183), carbon dioxide (0.845), hydrogen peroxide (1.04), laevulaldehyde (about 9.0), *n*-heptane- $\beta$ -dione (8.7), undecanetriene (0.9), pentadecanetetraone (0.06), unidentified ketonic fraction (8.29), resinous ketonic fraction (9.3), formic acid (about 18.3), laevulinic acid (about 12), succinic acid (1.5) [not formed in every case], hydrocheliconic acid (1.7), methyleyclohexenone-acetic acid (1.7), unidentified acid fraction (20), resinous acid fraction (6.4), resin from the ozonide (31.00). The production of the heptanedione by the decomposition of the ozonide is well in harmony with the cyclo-octadiene formula of caoutchouc, but not so that of the triketone and the tetraketone; these must be fission products of a larger ring. Moreover, since the heptanedione and the undecanetriene appear to be produced always in a definite ratio, both substances are probably generated by the oxidation of one and the same cyclic structure. Regarding the size of this structure, attention is called to the fact that the molecular weight in benzene of caoutchouc ozonide is 535 ( $C_{25}H_{40}O_{15}$  requires 580). Guided by this, and assigning to the natural caoutchouc molecule a  $C_{20}$ -ring, the necessity of a formula containing a repetition of the isoprene skeleton leads to the following formula for natural caoutchouc:—



The ozonide corresponding with this will yield only laevulaldehyde and laevulinic acid by its decomposition, but when the caoutchouc is converted through its hydrochloride into the regenerate I. a redistribution of the double linkings may occur by a shifting of two or more of the double linkings of the preceding formula of caoutchouc, the formation of the di-, tri-, and tetra-ketones, and of hydro



chelidonic acid is readily explicable. Regenerate I. can be converted through its hydrochloride into regenerate II.; the ozonide of the latter yields by decomposition with water a very much larger proportion of products of high h. pt. (compare Lichtenberg, following abstract) than does the ozonide of regenerate I. Consequently, in regenerate II., a renewed shifting of the double linkings must have occurred. In connection with the new formula of natural caoutchouc, it is noteworthy that the ozonide of "sodium isoprene caoutchouc," although exhibiting in freezing acetic acid a molecular weight corresponding with the formula  $C_{10}H_{16}O_4$ , yields amongst its products of decomposition acids of the formula  $C_{11}H_{18}O_4$  and  $C_{12}H_{20}O_4$ , and consequently must have a molecular formula at least  $C_{25}H_{40}O_{12}$ . A second phenomenon which is unfavourable to the  $C_5$ -ring formula of caoutchouc is the thermal dissociation of caoutchouc hydrochloride. When this compound is heated at  $100^\circ\text{C}$ . *in vacuo*, it loses hydrogen chloride until the percentage of chlorine has fallen to a value which remains constant at about 12.3. This value is of the same order of magnitude as that required if caoutchouc hydrochloride lost all but one of its moles. of hydrogen chloride.

*Caoutchouc hydrogen halides; Transformation products of— and their thermal dissociation.*  
O. Lichtenberg. *Annalen*, 1914, 408, 227—239.  
J. Chem. Soc., 1915, 108, i., 279—280. (Compare preceding abstract).

THE regenerate I. obtained from gutta-percha is not only very similar in external appearance to regenerate I. from caoutchouc, but its ozonide by decomposition with water yields formic acid, levulinic acid and its aldehyde, and *n*-heptane- $\beta$ -dione in proportions quite similar to those obtained in the case of the ozonide of regenerate I. of caoutchouc. Caoutchouc-regenerate I. forms a hydrochloride,  $C_{10}H_{14} \cdot 2\text{HCl}$ , pale brown mass, decomp.  $145^\circ\text{--}185^\circ\text{C}$ ., a bromide,  $C_{10}H_{14} \cdot \text{Br}$ , colourless powder, decomp.  $80^\circ\text{--}145^\circ\text{C}$ ., and a nitrosite,  $C_{10}H_{14} \cdot \text{O} \cdot \text{N}$ , yellow powder. Regenerate Ia, obtained by heating with pyridine the partly dechlorinated caoutchouc hydrochloride (preceding abstract), is pale brown, transparent, and very elastic. Caoutchouc-regenerate II., obtained from regenerate I. through its hydrochloride, is an elastic, violet-black substance, which is distinctly more soluble than caoutchouc in benzene and forms a hydrochloride, brown powder, decomp.  $135^\circ\text{--}185^\circ\text{C}$ ., bromide, brownish-white substance, decomp.  $115^\circ\text{--}145^\circ\text{C}$ ., nitrosite, yellow powder, decomp.  $130^\circ\text{--}135^\circ\text{C}$ ., and ozonide, golden-yellow, viscous oil. The decomposition of the last compound by water yields formic and levulinic acids, levulaldehyde, and *n*-heptane- $\beta$ -dione, together with a large quantity of unidentified substances of high b. pt. By prolonged boiling in toluene or xylene, caoutchouc undergoes a change of some sort, but still forms a hydrochloride.

*Caoutchouc; Swelling of—in organic liquids.*  
D. Spence and G. D. Kratz. *Kolloid. Zeits.*, 1914, 15, 217—226. J. Chem. Soc., 1915, 108, i., 280.

THE capacity to swell in contact with organic liquids is not common to all kinds of caoutchouc, but is limited to the raw material. Para caoutchouc, which has been washed, dried and rolled, is no longer capable of swelling, and this change in properties appears to be brought about even when the rolling has been continued for a very short period. Different samples of raw Para caoutchouc also exhibit considerable variations in swelling power. Circular discs of Para caoutchouc were immersed in various liquids and from time to time the change in dimensions of the discs and also the increase in weight were determined. If the

liquids are arranged in decreasing order according to the volume of liquid which is absorbed by 1 gm. of caoutchouc when the maximum swelling has been attained, the following series is obtained: (1) carbon tetrachloride and chloroform, (2) carbon bisulphide, (3) benzene, toluene, and xylene, (4) ether. Trichloroacetic acid in less than 1% concentration and acetic acid in less than 10% have no appreciable influence on the maximum swelling or on the velocity of the process, but at higher concentrations trichloroacetic acid increases both the maximum swelling and the velocity, and this effect increases with increasing concentration of the acid.

*Rubber; Depolymerisation of raw—.* A. van Rossem. *Rubber Industry*, London, 1914, 149—151.

ONE per cent. solutions of plantation Hevea crêpe in xylene were heated at  $130^\circ\text{C}$ . in a vessel connected with Hempel burettes, so that an absorption of gas could be measured accurately. The apparatus was so designed that a certain amount of gas could be passed through the solution while the total amount of gas in the apparatus remained constant. Samples of the solution could be withdrawn at any moment without air entering the apparatus. It was found that the viscosity of the solutions decreased considerably, but that no oxidation (indicated by absorption of gas) took place until after several hours heating. There is a "critical viscosity limit"—viz., about 1.6—1.3 viscosity-units for solutions of 1% concentration—at which oxidation of the solution begins. Reduction of viscosity proceeds more rapidly in an atmosphere of oxygen than in one of carbon dioxide. It is concluded that oxidation of rubber is always a secondary process, being preceded by depolymerisation, and that depolymerisation is accelerated catalytically by oxygen.—E. W. L.

*Vulcanisation; The mass action of sulphur in—.* H. Skellon. *Rubber Industry*, London, 1914, 172—177. (See this J., 1913, 876, 1022.)

MIXINGS of Para rubber and sulphur, containing the proportions of the latter indicated in the table, were vulcanised at  $140^\circ\text{C}$ . for various lengths of time, and the combined sulphur in the vulcanised products was determined by extracting in a Soxhlet apparatus for 20 to 60 hours and oxidising the dried rubber residue with fuming nitric acid. The figures given in the table show parts of combined sulphur per 100 parts of rubber:—

Vulcanisation, hrs.	3% S	5% S	10% S	20% S	30% S	40% S	50% S
1 .....	0.37	0.46	0.70	0.74	0.79	0.85	0.88
1 .....	0.47	0.66	1.19	1.31	1.36	1.38	1.32
14 .....	0.72	1.11	1.84	2.05	2.10	2.21	2.30
3 .....	1.46	2.17	3.72	5.09	5.11	5.22	5.62
6 .....	—	3.03	6.88	14.16	16.66	18.22	20.44
9 .....	—	—	9.73	21.65	34.13	42.5	50.0

Curves drawn by plotting total sulphur content against combined sulphur per 100 of rubber exhibit first an ascending portion and then a more or less flat portion, the points of inflexion corresponding to maxima in curves plotted with total sulphur content against combined sulphur per 100 of mixing. Up to these maxima the curves indicate that the amount of combined sulphur is proportional to the concentration of sulphur in the rubber. Beyond the maxima the rubber is saturated.—E. W. L.

*Rubbers; Use of nitric acid as a solvent for compounded and vulcanised—.* H. W. Jones. *Rubber Industry*, London, 1914, 189—190.

THE author suggests the use of nitric acid of sp. gr.



1.42 as a means of separating carbon-black from rubber, and of obtaining an indication of the presence of "hydrocarbons."—E. W. L.

*Bitumen in rubber mixings; Determination of*—B. D. Porritt and E. Anderson. Rubber Industry, London, 1914, 181—188.

NEITHER pyridine nor carbon bisulphide gives sufficiently trustworthy results when used as solvent for the determination of bitumen in rubber mixings. Attempts were made to effect a separation of the bitumen based upon the observation that it is apparently unaffected by heating with nitric acid (sp. gr. 1.355 at 19.1° C.) for 15 minutes at 100° C. A portion of the bitumen, however, is rendered insoluble in solvents by the action of the acid, and the method fails, partly, at least, for this reason.—E. W. L.

*Rubber goods;] Method of determining small amounts of carbon dioxide [in—], in presence of sulphides.* H. W. Jones. Rubber Industry, London, 1914, 191—192.

THE separated insoluble portion of the rubber sample is heated in a flask with 10 c.c. of hydrochloric acid and 10 c.c. of water. A current of air, free from carbon dioxide, is aspirated through the flask, and the carbon dioxide is collected in two flasks, the first containing 30 c.c. and the second 15 c.c. of the following reagent:—Barium chloride, 30 gms. in 180 c.c. of water; ammonia (sp. gr. 0.880) 36 c.c.; water "sufficient to measure 300 c.c." In this reagent sulphides are held in solution. The precipitated barium carbonate is rapidly collected, dissolved in hydrochloric acid, and converted into barium sulphate.—E. W. L.

*Mineral matter in vulcanised rubbers; A simple method for the determination of*—H. W. Jones. Rubber Industry, London, 1914, 199—201.

TWO grms. of the sample is heated with 40—50 c.c. of nitrobenzene in a 200—300 c.c. flat bottom flask, connected to a reflux air-condenser. When solution of the rubber is complete the flask is allowed to cool, the contents diluted with acetone, stirred with a glass rod, and allowed to stand. The mineral matter is deposited rapidly and is separated by decantation, transferred to a weighed filter-paper, and washed well with acetone. In some cases it is advantageous to wash further with alcohol and chloroform, and then to moisten the filter with water so as to obtain a moist and uncaked residue for further examination. Little or no carbon dioxide is eliminated from calcium or magnesium carbonate by boiling for one hour in nitrobenzene.—E. W. L.

*Rubber mixings; Determination of the mineral matter in*—B. D. Porritt and R. Wheatley. Rubber Industry, London, 1914, 193—199.

OZONE was passed over dry, powdered vulcanised rubber in a flask, which was shaken repeatedly in order to expose a fresh surface; the sample was then extracted with acetone, and the ash determined in the extracted residue. It was not found possible to render the whole of the organic matter soluble, and in many instances the mineral matter was chemically altered.—E. W. L.

#### PATENTS.

*India-rubber goods; Manufacture of vulcanised—embodying a foundation fabric.* W. E. Muntz, London. Eng. Pat. 3158, Feb. 6, 1914.

VULCANISED rubber goods, either before or after the formation of acids due to oxidation of the sulphur, are treated with an alkaline gas or vapour, either generated independently or from substances present in the goods. For example, the goods are immersed in gaseous or liquefied ammonia in a

closed vessel at about 17° C. and 7—15 atmospheres pressure for upwards of 5 minutes. The vessel is preferably exhausted before introducing the gas, and pressure applied afterwards. (See also Fr. Pat. 468,493 of 1914; this J., 1914, 974.)—E. W. L.

*Rubber, gulla-percha, and balata; Process for the separation of— from their latices.* H. Conoseus. Ger. Pat. 280,848, Nov. 13, 1913. Addition to Ger. Pat. 259,253 (see Eng. Pat. 22,255 of 1912; this J., 1913, 298).

THE latex is treated with such substances as will interact to form insoluble precipitates, a small amount of alkali being added simultaneously or subsequently if the substances added are neutral. The serum which separates from the coagulated rubber, etc., may be used to coagulate fresh portions of latex. Salts of alkaline-earth metals may be used and carbon dioxide employed for the precipitation.—C. A. M.

*Polymerisation products of butadiene, its homologues and analogous compounds; Process for the preparation of*—Badische Anilin und Soda Fabrik. Ger. Pat. 281,966, Aug. 2, 1913.

AN elastic compound, which swells up but is only sparingly soluble in the usual solvents, is obtained by polymerising the hydrocarbons at the ordinary or slightly increased temperature by the action of alkali metals or their mixtures or alloys, in the presence of metallic hydroxides or organic hydroxy compounds.—C. A. M.

#### XV.—LEATHER; BONE; HORN; GLUE.

*Tannin, and the synthesis of similar substances.* E. Fischer and K. Freudenberg. Ber., 1914, 47, 2485—2504. Chem. Zeit., 1915, 39, Rep., 123.

TURKISH tannin, prepared from dark Aleppo galls, contains ellagic acid and is much less homogeneous than Chinese tannin. The so-called glucogallie acid, or monogalloylglucose, isolated from Turkish tannin by Feist and Haun (this J., 1912, 1044), is a mixture of gallic acid and tannin; the Turkish tannin examined by the authors gave relatively more dextrose and less gallic acid upon hydrolysis with sulphuric acid, the proportions obtained pointing to the possible existence of a pentagalloylglucose in the tannin. A synthetic pentagalloylglucose was obtained by combining pure  $\beta$ -glucose with the chloride of tricarbomethoxy-gallic acid.—J. R.

*Tannins; Biological detection and valuation of*—R. Kobert. Ber. deuts. Pharm. Ges., 1914, 24, 470—495. Z. angew. Chem., 1915, 28, Ref., 155.

A SUSPENSION of red blood corpuscles washed free from serum was treated with solutions of tannin from gall-nuts. It was found that with a suitable quantity of tannin this was adsorbed practically completely from solution, and the blood corpuscles were agglutinated and settled to the bottom; on filtering, the blood corpuscles were retained on the filter, and the filtrate was colourless. When the tannin was recovered by treating the agglutinated blood corpuscles with hot alcohol, part was found to be converted into gallic acid. The latter has no agglutinating action, and the hydrolytic action of red blood corpuscles on tannin can be utilised to determine the tannin content of gall-nuts. With a 1% suspension of red blood corpuscles, complete agglutination was effected by pure tannin at a concentration of 1:25,000 and by the tannin of oak bark at 1:20,000. With Neradol the lowest concentration at which agglutination could be observed was 1:3300.—A. S.

*Analysis of lactic acid.* Balderston. See VII.

#### PATENTS.

*Di- and poly-hydroxybenzenes; Preparation of water-soluble condensation products of—.* Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 282,313, Nov. 19, 1913.

A di- or poly-hydroxybenzene, or a homologue or halogen substituted product, in which a *para*-position to a hydroxyl group is free, is dissolved in an indifferent solvent, and treated with acetaldehyde or its derivatives at a low temperature, with addition of acid or basic condensing agents. Water-soluble, syrupy products are obtained which tend to form crystalline substances, and combine with diazo-compounds. The products are of value as tanning materials and for the preparation of therapeutic substances. F. W. A.

*Drying [glue and like materials]; Apparatus and process for—.* W. J. Grosvenor, Grantwood, N.J. U.S. Pat. 1,138,751, May 11, 1915. Date of appl., April 9, 1909.

The air used as drying medium is circulated in a closed cycle, at one part of which it is purified by refrigeration, compression, and impingement against moist surfaces. At another point, the cool and moist air, at less than atmospheric pressure, impinges on the under surface of the glue to form a skin, and at another point, a horizontal current of drier air at a higher temperature and pressure passes over the glue, which is afterwards removed at a point where the pressure is above atmospheric. —W. F. F.

*Leather; Artificial—, and process of making the same.* L. Lilienfeld, Vienna, U.S. Pat. 1,110,171, May 18, 1915. Date of appl., July 11, 1911.

See Fr. Pat. 456,291 of 1913; this J., 1913, 953.

*Hides or skins; Method for preserving, stripping, and cleaning—.* R. Vidal, Asnières, France. Eng. Pat. 12,952, May 26, 1911.

See Addition of Aug. 21, 1913, to Fr. Pat. 135,917 of 1911; this J., 1915, 501.

### XVI.—SOILS; FERTILISERS.

*Soils; Determination of the sulphur-transforming power of—.* P. E. Brown and E. H. Kellog. J. Biol. Chem., 1915, 24, 73–89.

Soil-sulphide or free sulphur is added to the soil, the moisture content is adjusted to the optimum, and the mixture is incubated for 5–10 days at the ordinary temperature. Sulphates are then extracted by shaking the soil for 7 hours with water, precipitated with barium chloride, and their quantity determined by means of the sulphur photometer. The oxidation of sulphides and sulphur in the soil is brought about mainly by the action of bacteria; sulphides are slightly oxidised when shaken with water for 7 hours, but sulphur shows no change. The sulphur-transforming power of the soils tested varied with the treatment which they had previously undergone. Addition of manures increased the power, and, in general, soils poor in organic matter were low in sulphur-transforming properties. The water content of the soils also influenced the rate of oxidation of sulphur; the oxidation increased with increasing moisture until the optimum, or 50% of the amount necessary for saturation, was reached; further addition of water decreased the oxidation. Aeration up to a certain point, and admixture of sand up to 50% increased the oxidation of sulphur but the addition of carbohydrates to the soil resulted in a decrease in the oxidation. —W. P. S.

*Manganese compounds; Transformations of— in the soil under the influence of micro-organisms.* N. L. Sölingén. Zent. Bakt., 1914, [11], 40, 515. Chem.-Zeit., 1915, 39, Rep., 162.

The formation of manganic from manganous compounds in the soil depends on the microbiological oxidation of salts of organic acids to bicarbonates, and on the catalytic action of the salts of hydroxy-acids derived from the aerobic decomposition of carbohydrates. Manganic oxides are always converted into manganous compounds when hydrogen sulphide, nitrous acid, peroxides, oxydases, peroxydases, and reductases, or hydroxy-acids are also present. Hydroxy-acids are only produced from cellulose by aerobic decomposition, so that manganous-cellulose discs can be used to determine the number of organisms decomposing cellulose aerotically, which are present in soils. Filter paper is coated with manganic oxide by dipping in manganous sulphate solution and then in permanganate solution. The cellulose-decomposing organisms are thus shown as white spots on the brown background of manganic oxide. Manganic oxides, including finely ground natural manganese minerals, assist aerobic conditions in agricultural soils by removing hydrogen sulphide. In acid soils they convert nitrous acid into the readily assimilable manganese nitrate, destroy deleterious peroxides, etc. The fixation of nitrogen by azotobacter in presence of cellulose is to be attributed to the effect of the calcium salts of hydroxy-acids rather than to the presence of fatty acids. T. C.

*Manganese in soils; Determination of—.* B. von Horváth. Z. anal. Chem., 1914, 53, 581–593. J. Chem. Soc., 1915, 103, ii., 285.

The colorimetric method described by Marshall, depending on the oxidation of manganous salts to permanganate by ammonium persulphate in the presence of silver nitrate (compare Schowalter, this J., 1914, 570), is recommended for the estimation of manganese in soils. The hydrochloric acid extract of the soil is twice evaporated to dryness with nitric acid to expel chlorine and destroy organic substances, the residue is then heated with sulphuric acid to remove the nitric acid, and the process proceeded with as described. Gravimetric and volumetric methods were found to be trustworthy for the purpose.

*Soil bacteria; Culture media for use in the plate method of counting—.* H. J. Conn. New York Agric. Expt. Stat., Bull. No. 38, Nov., 1914, 34 pages.

An ideal culture medium should allow a maximum number of bacteria to develop, should permit of a differentiation between different kinds, and should contain materials of definite composition, thus ensuring uniformity in the counts. A new soil-extract gelatin medium fulfils the two first conditions, and a new sodium asparaginate agar medium complies with the first and third. The former contains 100 parts of soil-extract, 120 of gelatin, 1 of dextrose, and 900 of distilled water, and its reaction should be 0.5% N 1 acid, using phenolphthalein as indicator. The agar medium is composed of 12 parts of agar, 1 of sodium asparaginate, 1 of dextrose, 0.2 of magnesium sulphate, 1.5 of mono-ammonium phosphate, 0.1 each of calcium and potassium chlorides, and 1000 of water. The dextrose and asparaginate are added immediately before sterilisation. Clarification is best effected by steam-heating for 30 mins. and decanting through cotton-wool. The product should require 0.8–1.0% of N 1 acid. The incubation periods are 7 days and 10–14 days respectively, and the temperature 18° C. for both. The agar medium gave quantitative results fully

equal to those of other agar media usually employed. For qualitative work gelatin media are preferable. —E. H. T.

*Soil: Bacteria of frozen* ——. H. J. Conn. New York Agric. Expt. Stat., Bull. No. 35, July, 1914, 20 pages.

The number of bacteria in a silty clay loam soil was found to increase appreciably when the soil had been frozen for 15 days or more. As the soil was in pots, the increase was not due to bacteria from subsoil. The same effect of frost was observed in the soil in the field. A rise in moisture content was usually followed by a rise in the bacterial number in aerated or non-aerated, frozen or unfrozen soils. Soil that had been recently aerated contained many more bacteria than macerated soil. —E. H. T.

*Fertiliser soils: Absorption of* —— by Hawaiian soils. W. McGeorge. Hawaii Agric. Expt. Stat., Bull. No. 35, Aug. 21, 1914, 32 pages.

The soils of Hawaii are of a strongly basic nature, and the concentration of the highly basic soil solution depends upon the absorptive power of the soil, not upon the solubility of the mineral constituents nor upon the amount of fertiliser added. The absorptive power is influenced greatly by the presence of accumulated humus. Tests were made with a sandy soil rich in magnesia and low in organic matter, a yellow clay, a poor sandy soil, a very productive light soil, and a heavy, red, highly ferruginous clay which is very abundant in the islands. The absorptive powers of these soils were determined by adding mineral solutions to 100 grms. of each, confined in glass tubes of 1-inch diameter, fitted with rubber stoppers and pinchcocks to regulate the flow. The absorption of phosphoric acid from monopotassium and monocalcium phosphate was very great, and the former had a decided deflocculating effect on the clay. The fixation of potassium was marked but less than that of phosphoric acid; it was largely influenced by the amounts of calcium and potassium present. These same factors also controlled the absorption of ammonium-nitrogen. The heavy red clay soil absorbed considerably less phosphate, potash, and ammonium-nitrogen than the other soils. Only highly organic soils exerted any absorbent effect upon nitrogen present as nitrate, but a fresh soil absorbed better than an air-dried soil. Phosphoric acid and ammonium-nitrogen were fixed better by a fresh soil, and potassium by an air-dried soil. Except in the case of nitrates the absorption in the subsoil was better than in the surface soil. Solutions of mixed fertilisers percolated more rapidly than solutions of single fertilisers, hence the application of mixed artificial fertilisers is wasteful. Heat and antiseptics did not influence the absorption to any marked extent. —E. H. T.

*Humus: Acids and colloids of* ——. G. Fischer. Kuhn-Arch., 1914, 4, 1—136. J. Chem. Soc., 1915, 108, i, 217.

Colloidal substances were isolated from peat and from cultivated black soil by extracting with cold or hot water, filtering the solution through hard-ened paper filters, concentrating it *in vacuo* at 50° C., and purifying it by dialysis through parchment. The total ash amounted to 8.6–23.3% of the dry matter of the colloidal substance. The mineral substances present were iron, calcium, potassium, and sodium, and small amounts of magnesium and phosphorus; alumina, manganese, and silica were absent. Unlike the reversible organic colloids, the humus colloids were found to be without protective action on gold hydrosols.

*Soil analysis: Vegetation experiments and* ——. O. Lemmermann. Landw. Versuchs-Stat., 1914, 85, 147–154. J. Chem. Soc., 1915, 108, i, 364.

Two different soils yielded, in three weeks, carbon dioxide corresponding with 13% and 3.5% respectively of the carbon content of the soil. When the soils were mixed with sand so that both mixtures contained the same amount of organic matter, the amounts of carbon dioxide produced were 19% and 15%. The different rates of decomposition depended, therefore, on the character of the soils rather than on the nature of the organic matter. The best method of extracting soils, for estimating solubilities, seems to be continuous percolation of the solvent. This should be possible even with heavy soils, if these are mixed with sand.

*Phosphoric acid in soil extracts [containing titanium]; Determination of* ——. L. G. den Berger. Intern. Milt. Bodenk., 1914, 4, 46. J. Chem. Soc., 1915, 108, ii, 278.

An aliquot portion of the hydrochloric acid extract is diluted, boiled, and treated with a slight excess of ammonia. The precipitate is washed twice with hot water, dried on the filter, ignited in a platinum crucible, and fused with 2–4 parts of anhydrous sodium carbonate. It is then extracted with cold water, filtered, and washed until 20 drops of the filtrate gives no residue when evaporated. The residue contains ferric oxide, and all the titanium in the form of sodium hydrogen titanate. The filtrate, which may be turbid owing to ferric oxide passing through, is acidified with nitric acid until the ammonia at first precipitated re-dissolves, evaporated down, and the phosphoric acid estimated in the usual manner.

*Phosphoric acid in vegetable products and soils; Iodometric determination of* ——. J. Preisinger and F. Frodl. Z. landw. Versuchs., Oester., 1914, 47, 92. J. Chem. Soc., 1915, 108, ii, 278–279.

The substance (10–20 grms. of hay or straw, etc.) is left overnight with fuming nitric acid (20–25 c.c.), and then heated with strong sulphuric acid (10–15 c.c.) until all the brown fumes are expelled. Nitric acid is then added until the solution is colorless, or slightly yellow. The solution is diluted to 200 c.c., and after the silica has settled, 20–25 c.c. is withdrawn, diluted to 40–50 c.c. with nitric acid, sulphuric acid, and water, so as to contain 1–1.5 c.c. of strong sulphuric acid and 10 c.c. of strong nitric acid, and precipitated by Lorenz's method. The precipitate is left, according to the amount, for two to eighteen hours, filtered, and washed with tap-water until free from sulphuric acid, and is then transferred, along with the filter, to somewhat diluted bromine containing a little N/2 sodium hydroxide, rubbed with a glass rod and diluted to 200–300 c.c. Sodium acetate (5 grms.) and potassium iodide (0.5–1 gm.) followed by a few c.c. of N/4 sulphuric acid to precipitate the iodine, are then added, after which the iodine is titrated with thiosulphate solution in presence of starch solution. One c.c. of N/10 thiosulphate = 0.000761 gm. P<sub>2</sub>O<sub>5</sub>. The bromine solution is prepared by adding 1100 c.c. of bromine water to a cooled N/4 sodium hydroxide solution (500 c.c.). The titration can be done by artificial light.

*Farmyard manure*. R. A. Berry. West of Scotland Agric. College, Bull. No. 65. J. Board Agric., 1915, 22, 131–135.

During the winter months in the west of Scotland the average loss in weight of 8-ton heaps of farmyard manure was 20.6% in the open and 17.5% under cover. Unprotected manure lost 8% more nitrogen than protected, and over 20% of the phosphoric acid and potash, the loss of these in

manure kept under cover being negligible. The average difference of crop-increase for potatoes and turnips was 7% in favour of the manure stored under cover. The loss in weight of exposed cow, pig, bullock, and horse manure (with straw and with peat-moss litter) was 22.3% for the whole; it was much less for horse manure with peat-moss than with straw. The average losses during rotting were: nitrogen 29.6%, phosphoric acid 12.2%, potash 33.5%, organic matter 32%. The effect of rotting was to lower the value of the manures regarded as plant-food, and the crop results showed that the fertilising values were accurately indicated by the chemical analyses. Gypsum and sodium bisulphate were most effective in fixing the ammonia, whereas superphosphate, kainit, and calcium carbonate increased the loss. Farmyard manure applied in the drills to potatoes and turnips in spring, gave a crop-increase of 56% when fresh, 42% when rotted; 9% of these gains was due to the manner of application. Applied broadcast in autumn, the crop-increase was 25%. Ploughing-in in autumn on the turnip field gave a gain of 5% as against broadcasting. On the other hand, the residual value of the manure applied in autumn was greater than that used as a spring-dressing, and it was greater for potatoes than for turnips. When the land was spring-dressed, 18% of the nitrogen was recovered in the crops, but with autumnal dressing only 9%. —E. H. T.

*Farmyard manure; Storage of.* — F. Lohms and J. H. Smith. *Fühlings Landw. Zeit.*, March 1, 1911. *J. Board Agric.*, 1915, 22, 138.

To conserve the full nutrient value of farmyard manure, the solid and liquid portions should be collected and stored separately, the latter preferably in peat-moss. The value of the dung and straw fraction is due to its high bacterial content and richness in humus; its nitrogen is but slowly mineralised. The nitrogen of the separated liquid portion is as readily available as that in ammonium sulphate or sodium nitrate. Ordinary farmyard manure often exerts a better effect than the urine-free manure, but the advantage does not persist beyond the first year, and it is more than neutralised by the loss during storage and the incomplete utilisation of the fertilising constituents of the urine. —E. H. T.

*Horse manure; Destruction of house-fly larvæ in.* — E. C. Cook, R. H. Hutchison, and F. M. Seales. *Bull. U.S. Dept. Agric.*, No. 118, July 11, 1911, 26 pages.

The most effective, economical, and practical means of destroying incipient fly life in horse manure (and other habitats), is by treatment with borax and water. For 10 cub. ft. (8 bushels) of manure, 0.62 lb. of powdered borax is applied around the outer edges of the heap, which are then sprinkled with 2–3 gallons of water, the treatment being repeated when fresh manure is added to the heap. Although killing over 99% of the fly larvæ, the treatment does not permanently affect the bacteria in the manure; it causes an increase in the water-soluble nitrogen and the ammonia. As borax-treated manure has not been tested on all crops, its application in dressings of over 15 tons to the acre is not recommended. The cost of treatment is about 1d. per horse per day. Calcined columbite (crude calcium borate), being much less soluble, is also less effective; it kills many larvæ, but, unlike borax, it does not destroy the eggs. Ferrous sulphate is larvical but injures the manure. The other substances investigated, e.g., kerosene, copper sulphate, cyanide, Paris green, cyanamide, were either too poisonous a nature or ineffective. —E. H. T.

*Potash; Saw-mill waste as a source of.* — C. T. Gimingham. *J. Board Agric.*, 1915, 22, 146–148.

In some mills wood-scrap, sawdust, and shavings are used as fuel, either alone or mixed with coal, but a very large amount is still available for conversion into ash. Analyses of ash samples show that dust from boiler-flues and chimneys, which is dry and in good mechanical condition, contains the most potash (up to 10%  $K_2O$ ), whilst ordinary coarse ash contains less (5–7%  $K_2O$ ). On the basis of the normal price of kainit, these ashes would fetch from 25 to 50s. per ton, and timber-merchants would profit by erecting plant to burn their scrap. —E. H. T.

*Vanillin; Field test with a toxic soil constituent.* — J. J. Skinner. *Bull. U.S. Dept. Agric.*, No. 164, Jan. 30, 1915, 9 pages. (See also this J., 1911, 1164.)

A poor culture of clover sown in a moderately fertile loam soil containing added vanillin, attained a healthy but very stunted appearance, the weight of the green crop being less than one-half that of the control. The harmful effect of vanillin on wheat in pots was very marked in two cases where the soil was poor, but was not observed in the case of a productive loam. The growth and yields of cowpeas, string beans, and garden peas, tested under field conditions in a silty clay loam soil of an acid nature, were much inferior to those of similar plants grown in untreated soil, the crops of cured hay, marketable beans, and peas, showing a reduction of 39, 69, and 20% respectively. Vanillin was detected in the soil of each crop six months after application. The three soils were then used again for similar plants cultivated in the greenhouse for 26 days. The relative growths were 71, 71, and 94% of plants grown in normal soil. Wheat plants cultivated in the same three soils showed an average reduction in green weight of 73%. —E. H. T.

*Phosphoric acid; Use of sodium citrate for the determination of reverted.* — A. W. Bosworth. *New York Agric. Exp. Stat., Tech. Bull. No. 34*, May, 1911, 10–12.

The use of a solution of sodium citrate instead of neutral ammonium citrate for the determination of reverted phosphoric acid in phosphates is recommended. Sodium citrate solution gives more concordant results than ammonium citrate, and the latter suffers also from the disadvantage that loss of ammonia occurs during the determination. —A. S.

*Determination of sulphuric acid and potassium, especially in potash salts.* Vanabel. *See VII.*

*Quassia as a contact insecticide.* Parker. *See XIXB.*

#### PATENT.

*Mono-calcium phosphate; Process of producing.* R. Stewart, Logan, Utah. *U.S. Pat.* 1,137,806, May 4, 1915. Date of appl., June 17, 1911.

Phosphoric rock is submitted to the action of sulphur fumes in the presence of steam in a rotary furnace. The solution containing mono-calcium phosphate and calcium bisulphite thus obtained, is oxidised electrolytically to convert the bisulphite into calcium sulphate and sulphuric acid, and the solution is concentrated to recover the acid phosphate. —H. R. D.

## XVII.—SUGARS; STARCHES; GUMS.

*Sugar maple: Organic acids from the sap of the* ——. E. O. von Lippmann. Ber., 1911, 47, 3091—3095; 1915, 48, 288. J. Chem. Soc., 1915, 108, i, 362.

THE scale which forms on the walls of the evaporating pans in the manufacture of maple sugar (so-called "sugar sand") was found to contain *l*-malic, *d*-tartaric, and tricarballic acids. (See also this J., 1911, 480; 1911, 508.)

*Sugar, dextrin, and starch solutions: Effect of clarification with lead tamate in the polarimetric examination of* ——. A. Grossfeld. Z. Unters. Nahr. Genussm., 1915, 29, 51—53. Z. angew. Chem., 1915, 28, Ref., 223.

SOLUTIONS of sugar and of dextrin can be clarified for polarimetric examination by means of tannin and lead acetate; the polarisation of sugar solutions is not appreciably affected by the treatment; dextrin is adsorbed by the precipitate to some extent, but the error thus caused is negligible in the case of concentrated solutions, provided only a small quantity of clarifying agent is used. The method is not applicable to starch solutions, as a considerable quantity of starch is absorbed by the lead tamate precipitate.—A. S.

## PATENTS.

*Sugar juices: Centrifugal device for filtering* ——. L. G. G. Dilberts, Cagnas, Porto Rico, U.S. Pat. 1,138,608, May 4, 1915. Date of appl. Apr. 6, 1914.

THE casing of the centrifugal has two diametrically opposed discharge openings, and means are provided for tilting the casing so that the liquid may be discharged through either of the openings. J. F. B.

*Syrup: Production of a high-grade* ——. O. Giess. Ger. Pat. 282,810, Nov. 9, 1913.

A SYRUP in which the ratio of sucrose to invert sugar is 5:2, does not crystallise or become turbid on keeping.—A. S.

## XVIII.—FERMENTATION INDUSTRIES.

*Yeast: Influence of organic acids on* ——. I. Buronsky. Zentr. Bakt., II. Abt., 1911, 42, 530—557. Z. angew. Chem., 1915, 28, Ref., 150—151.

WHEN yeast is grown in a mineral nutrient solution to which peptone and an organic acid are added, no zymase is formed, but the quantity of oxidising enzyme increases, especially when succinic acid is used. After continued cultivation in such media, the yeast becomes acclimatised and then multiplies more rapidly than at first. If the yeast now be transferred to a medium containing sugar it multiplies more rapidly than in the acid medium, and after 1–3 days it begins to ferment the sugar, though only very slowly at first. In other words the loss of fermenting power extends to several generations but is ultimately regained; hence there is no mutation of the kind specified by De Vries. The rate of multiplication of the yeast in the acid media and in presence of sugar, and the speed with which fermenting power is regained, both vary according to the acid used, being greatest with quinic acid and least with tartaric acid.—A. S.

*Yeasts: Influence of organic acids on* ——. II. Zikes. Allgem. Zeits. Bierbrau., 1915, 43, 1–4. Z. angew. Chem., 1915, 28, Ref., 151.

THE author has shown previously that a potato-water-gelatin medium to which considerable

quantities of acid are added, may be used to separate yeasts from bacteria. Thirty different yeasts and eighty different kinds of bacteria were examined, and all of the former were capable of withstanding 2% of free lactic acid, whereas the latter were scarcely capable of withstanding 0.25%. Lactic acid at a concentration of 0.2–1% acts as a stimulant to yeast, as also do small quantities of tartaric acid, especially towards typical wine yeasts. Yeasts are much less resistant to butyric acid. Acetic acid gives different results according to the kind of yeast: beer yeast is relatively very sensitive, whereas *Mgeoderm* are capable of directly assimilating the acid. The effect of acetic acid on wine yeasts can be diminished by vigorous aeration. Formic acid at 0.4% concentration has an injurious action on beer yeast in wort media. Oxalic acid in 1% solution inhibits the fermenting power of yeast within 24 hours, and in 10% solution kills the yeast within 5 minutes.—A. S.

*Reductase of yeast*. S. Loxv. Biochem. Zeits., 1914, 66, 140–166. J. Chem. Soc., 1915, 108, i, 357–358.

THE relationship between the amount of methylene blue reduced, and the amount of carbon dioxide evolved under various conditions of fermentation, was investigated. The methylene blue was determined by titration with titanium chloride. It was found that for every two mols. of phosphate added to the fermentation mixture, one additional molecular equivalent of methylene blue was reduced. It is suggested that the withdrawal of two atoms of hydrogen from the fermentation mixture under the influence of the reductase converts the complex organic phosphorus compounds, to which the reduction is due, into another product, which is not in the position to bring about reduction. It is not yet decided whether it is the primary organic phosphorus compound formed in the fermentation mixture before the conversion of the hexose into alcohol and carbon dioxide, or the secondary product, the hexose phosphate, which acts as the reducing agent. The addition of sugar in the experiments with dried yeast caused in the first hours of fermentation a doubling of the amount of reduction, which was not observed when maceration juice was employed. This is due probably to the presence of free phosphates in the maceration juice and their absence in the dried yeast. The experiments indicate generally the importance of the reductase in the fermentation process. The two factors, which are necessary for fermentation, and which are removed by dialysis or washing of the yeast, are also necessary for the reduction process.

*Invertase. III. Influence of temperature on the "invertase content" of yeast*. J. Meissner and L. Somper. Biochem. Zeits., 1914, 67, 361–381. J. Chem. Soc., 1915, 108, i, 358.

TEMPERATURE plays an important part in the enrichment of the invertase in yeast when the organism is allowed to grow in sugar solutions. After twenty-four hours in the beer mash at 25°C. the "invertase content" is increased four- to five-fold. The optimum temperature for the increase in the mash is about 30°C., but in pure sugar solutions it is about 25°C. A similar increase is not observed when the yeast is kept in water at 25°C., nor is it observed to any extent when kept in sugar solutions at low temperatures. The increase in invertase content is more or less independent of the strength of the sugar solution, and is thus independent of the growth of the organism. Yeast grown on levulose showed a larger increase in the invertase than that grown on dextrose.

**Fermentation of dextrose; Influence of certain acids of biological importance (pyruvic, lactic, malic, and tartaric acids) on the —.** C. Nenberg and L. Czapski. *Biochem. Zeits.*, 1911, **67**, 51-55. *J. Chem. Soc.*, 1915, **108**, i, 359.

The inhibitory action of the above acids on fermentation of the sugar with various races of yeast is in all cases less than that of acetic acid.

**Carboxylase in the juice of top yeasts.** C. Nenberg and L. Czapski. *Biochem. Zeits.*, 1911, **67**, 9-11. *J. Chem. Soc.*, 1915, **108**, i, 355.

It is possible to prepare from top yeasts a juice containing a carboxylase which will act both on pyruvic and oxalacetic acids. In the experiments, a commercial dried yeast known as "Florylin," was employed.

**Life and fermenting power; Chemical means of separating —.** T. Bokorny. *Allgem. Brauer. J. Hopfenzeit.*, 1913, 53. *J. Chem. Soc.*, 1915, **108**, i, 360.

The zymase of yeast cells is more resistant to poisons than the plasma. In 0.1-0.5% sulphuric acid yeast cells are killed, but not the zymase. Similar results were obtained with 1% iron sulphate. Potassium chlorate (2-5%) inhibits growth, but not fermentation. Separation of life and fermenting power was also obtained with ammonium fluoride (1-0.1%), potassium and ammonium oxalates (1-0.1%), and formaldehyde (0.1%).

**Formaldehyde; Conversion of — into methyl alcohol. Phytochemical reductions. VIII.** C. Nenberg and E. Welde. *Biochem. Zeits.*, 1911, **67**, 101-110. *J. Chem. Soc.*, 1915, **108**, i, 355-356.

The formation of methyl alcohol from formaldehyde when the latter is added to a fermenting mixture of sugar and yeast is confirmed. A yield of about 15% was obtained, the methyl alcohol being estimated in the mixture of methyl and ethyl alcohols by oxidation and colorimetric determination of the formaldehyde formed. The reduction of the aldehyde to the alcohol appears to take place only in the presence of the living yeast.

**Enzyme action; Surface tension and —.** E. Beard and W. Cramer. *Roy. Soc. Proc.*, 1915, **88b**, 575-583.

The inversion of 20% sucrose solutions by small quantities of invertase was found to be perceptibly retarded by the presence of a number of small glass beads in the liquid, i.e., by increasing the surface of the system. The retardation is attributed in part to the fact that the enzyme is "surface active" and therefore tends to concentrate at the surfaces, whereas the sugar remains uniformly distributed throughout the liquid. Preliminary experiments indicate that the phenomenon is not confined to invertase. —J. H. L.

**Amylase of potatoes. Plant enzymes. II.** G. Doby. *Biochem. Zeits.*, 1911, **67**, 166-181. *J. Chem. Soc.*, 1915, **108**, i, 362-363.

AMYLASE is always present in the juice of the resting tuber, but the amount is less than that in cereals. The optimum temperature of its action is 40°C., which is less than that of many other plant amylases. Sodium fluoride is a good activator. Sodium chloride and mono- and di-potassium phosphates exert an inhibitory action. Potassium nitrate is without action. Hydrogen and hydroxyl ions in small concentrations activate, but in large concentrations inhibit the enzyme action. The

boiled potato juice has also an activating action. Juice which has been filtered through porcelain loses its activity. The activity is inhibited by sugars in the following (increasing) order: mannose, galactose and sucrose, arabinose, levulose and lactose, dextrose and maltose. The fission products of the enzyme possess, therefore, the greatest power of inhibiting its activity. (See also this J., 1915, 568.)

**Tartaric acid in beverages, especially in wines; Determination of —.** E. P. Häussler. *Z. anal. Chem.*, 1911, **53**, 542-560. *J. Chem. Soc.*, 1915, **108**, ii, 291.

EXAMINATION of various methods showed that Halenke and Moslinger's method (*Z. anal. Chem.*, 1891, **34**, 279) yields trustworthy results, but in the case of beverages containing but little, if any, tartaric acid, the correction of 0.225 grm. of tartaric acid is misleading. Villiers and Collins' modification of Berthelot and Fleuriot's method (precipitation of the tartaric acid by the addition of potassium bromide and alcohol, and titration of the resulting potassium hydrogen tartrate) is also trustworthy, even in the case of slightly plastered wines. The racemate method (this J., 1910, 451; 1912, 951) was only applied in a few cases, and its accuracy was not definitely ascertained; it appears to be tedious and costly.

**Methyl alcohol in brandies; Origin of —.** T. von Fellenberg. *Mitt. Schweiz. Ges.-Amt*, 1914, **5**, 172. *Chem.-Zeit.*, 1915, **39**, Rep., 67.

BRANDIES prepared from grape juice fermented in presence of the marc contain more methyl alcohol than those from juice fermented after removal of the marc. It is concluded that the pectin and protopectin contained in the marc produce methyl alcohol, under the influence of pectase, during fermentation. In an investigation of a number of cellulose drugs (*Membranindrogen*) methoxy-groups were found only in the celluloses (ligno- and pecto-membranins) containing polysaccharides and in gum tragacanth; those drugs which contained no polysaccharides were free from methoxy-groups. —J. H. L.

**Tannins for liqueurs; Adulteration of —.** F. Repiton. *Ann. Falsif.*, 1915, **8**, 118-123.

TANNINS extracted with alcohol or ether from galls are used in the preparation of vermouth and other liqueurs. They contain 82 to 86% tannic acid and 12 to 14% moisture, and are soluble in 95% alcohol. A commercial sample treated with 95% alcohol left a crystalline deposit, which was identified as sucrose. The hide-powder method is recommended for the determination of tannic acid. —C. A. M.

**An adulterant of crude and refined tartarates.** Charles. See VII.

#### PATENT.

**Mash-filter plat.** J. Schacter, Frankfurt, Germany. U. S. Pat. 1,438,251, May 1, 1915. Date of appl. July 30, 1913.

Is a mash filter-press composed of grains-cake frames and water-chamber frames, the filter cloths are supported by bars extending upwards from the base of each water-chamber frame in divergent planes, so that the cakes of grains have a trapezoidal cross section, thicker at the base than at the top, the bottom portion extending into the water-chamber frames beyond the limits defined by the edges of the frames. The grains-cake frames are constructed with a triangular prismatic floor forming a groove in the bottom of the cakes to facilitate their removal. —J. F. B.

## XIXA.—FOODS.

*Milk of cows; Cause of acidity of fresh —, and a method for the determination of acidity.* L. L. Van Slyke and A. W. Bosworth. New York Agric. Exp. Stat., Tech. Bull. No. 37, Dec., 1914, 4—6.

IN the determination of the acidity of whole milk by titration with alkali in presence of phenolphthalein, the calcium should first be precipitated by treating 100 c.c. of the milk with 2 c.c. of a saturated solution of neutral potassium oxalate; otherwise high results are obtained because dialcium phosphate, present in the milk and formed during titration, is hydrolysed to form calcium hydroxide and phosphoric acid, and the calcium hydroxide reacts with more dialcium phosphate to form tricalcium phosphate. If whole milk be titrated direct, about twice as much alkali is required as when the serum obtained by filtering the milk through a porous porcelain filter is titrated. This discrepancy is due, not, as is ordinarily assumed, to the acidity of milk casein, but to retention of dialcium phosphate by the filter; casein is present in fresh milk as a calcium caseinate neutral to phenolphthalein.—A. S.

*Milk; Effect of sodium citrate in preventing curdling of — by rennin.* A. W. Bosworth and L. L. Van Slyke. New York Agric. Exp. Stat., Tech. Bull. No. 34, May, 1914, 3—9.

THE curdling of milk by rennin is retarded or prevented by addition of sodium citrate. No curdling takes place when the quantity of sodium citrate reaches 0.4 gram. per 100 c.c. (1.7 grains per oz.), and with smaller quantities, the softness of the curd increases with the quantity of citrate. The effect is due to a reversible reaction between the sodium citrate and the calcium caseinate of the milk, with formation of calcium-sodium caseinate, which latter yields a soluble calcium-sodium paracaseinate by the action of rennin.—A. S.

*Casein; Action of rennin on —.* A. W. Bosworth. New York Agric. Exp. Stat., Tech. Bull. No. 37, Dec., 1914, 10—11.

SPECIMENS of pure paracasein prepared from fat-free milk by the action of rennin and of trypsin respectively, were found to have the same percentage composition, identical with that of pure casein (this J., 1913, 669). This proves that in the production of 2 mols. of paracasein from 1 mol. of casein by hydrolysis, there is no cleavage of any of the elements contained in the original casein molecule. It is probable that the cleavage of nitrogen, phosphorus, and calcium, stated by Harden and Macallum (Biochem. J., 1914, 8, 90) to occur when caseinogen is converted into casein by enzyme action, follows rather than accompanies this conversion.—A. S.

*Clotted cream.* W. Sadler. J. Board Agric., 1915, 22, 105—116.

THE addition of water to the milk before the pans are set to separate the cream, is found to act adversely on the flavour, texture and keeping quality, and it does not affect the fat-content or add to the actual weight of the cream. The value of the scald milk is also lowered, and the amount of sediment remaining in the pan is not diminished. With a suitable rich milk, clotted cream can be made in any locality, due care being taken to maintain during scalding a uniform temperature of 180—185° F. (82—85° C.) for a uniform time (25—30 min.). The yield is about 1 lb. of cream from 20.5—23 lb. of milk. The flavour and keeping quality are mostly determined by bacteriological factors. Cream with a characteristic flavour is made by scalding for 1½—2 hours over the glowing embers of a peat fire. Samples of

clotted cream investigated kept well for 36, 48, and 60 hours respectively after skimming.

—Es H. T.

*Milk; Alcohol reaction of —.* A. Auzinger. Molk. Zeit., 1911, 23, 457. J. Chem. Soc., 1915, 108, ii., 293. (See this J., 1911, 1106.)

NORMAL milk to which a small amount of fresh rennet has been added, gives a precipitate at once with 68% alcohol, indicating that rennet causes an immediate change in milk, liberating calcium salts. The greater the amount of soluble calcium salt present, the sooner is coagulation produced by alcohol. Most single samples of milk fail to coagulate with alcohol after being boiled, if the acidity is normal. Addition of various substances, such as sodium fluoride, ammonium oxalate, formaldehyde, etc., interferes with the alcohol test; substances which precipitate calcium prevent coagulation, whilst soluble calcium salts increase coagulation. The milk of cows fed with calcium phosphate is coagulated with alcohol of lower concentration than milk from control cows. Alcohol of 70% by vol. is recommended.

*Lecithin in milk; Methods of determination of —.* N. A. Brodick-Mitard. Biochem. Zeits., 1914, 67, 382—390. J. Chem. Soc., 1915, 108, ii., 293—294.

BUROW'S method (Z. physiol. Chem., 1900, 30, 495) of determining lecithin in milk consists in dropping the sample into a mixture of equal parts of alcohol and ether acidified with acetic acid, evaporating the filtrate at a low temperature, extracting with dry ether, and determining the phosphorus in the ethereal extract. The process is liable to give inaccurate results if the evaporation residue is not dried before extraction; drying is conveniently effected with anhydrous sodium sulphate.

*Cheese; Ripening of Neufchâtel —.* O. LANA. Z. Unters. Nahr. Genussm., 1914, 28, 387—392. Z. angew. Chem., 1915, 28, Ref., 12.

THE ripening of Neufchâtel cheese is brought about by practically the same kind of aerobic organisms that cause the ripening of Camembert cheese; the growth of the organisms on the surface of the cheese is accompanied by the formation of enzymes which pass into the interior and hydrolyse the proteins. Casein is the principal protein attacked, and it is converted into albumoses, peptones, ammonia, and volatile acids; in the inner portions of the cheese albumoses and peptones predominate and only small quantities of amides are found. Ammonia is distributed uniformly throughout the cheese. The greater decomposition which takes place in the outer layer of the cheese causes an increase in the quantities of fat and ash in this portion.—W. P. S.

*Lupin seeds; Composition and effects of — added to enzymes. Detection of lupin seeds in admixture with castor oil seeds.* G. Munk. Landw. Versuchs Stat., 1911, 85, 393—416. Bull. Agric. Intell., 1915, 6, 113—111.

BESIDES a diastatic enzyme and others which respectively decompose glucosides and peptones and produce changes in urea, lupin seeds contain an enzyme, hitherto unknown, which converts starch and certain sugars into lactic acid. Blue lupin seeds also contain a non-toxic, agglutinating enzyme which is rapidly destroyed at 70—75° C. This fact may be utilised to detect their admixture with castor-oil seeds, since the ricin of the latter is not affected at this temperature. E. U. T.

*An adulterant of crude and refined tartrates.* Carles. See VII.

## PATENTS.

*Milk; Condensed* — [containing other food substances]. J. M. C. L. Renard, Blois, France. Eng. Pat. 10,588, April 29, 1914.

MILK, before or after concentration, is mixed thoroughly at 100° C. with a suitable proportion of coffee, chocolate, tea infusion, Japan glue, or gelatin, and the mixture is sealed in tins. Flavouring substances, such as vanilla, almond, or lemon, may also be added. (Reference is directed to Eng. Pats. 897 and 1596 of 1876, 3087 of 1877, 1315 of 1882, and 15,387 of 1885).—W. P. S.

*Milk; Method of pasteurising* —. H. Feldmeier and C. B. Dalzell, Assignors to D. H. Burrell and Co., Little Falls, N.Y. U.S. Pat. 1,138,097, May 4, 1915. Date of appl., June 9, 1911.

MILK is passed rapidly in a stream of small cross-sectional area through a heater where it is heated to a pasteurising temperature, then flows slowly through a pasteurising apparatus, and afterwards through a cooling apparatus.—W. P. S.

*Milk powder; Process of producing soluble* —. G. D. Harris and J. S. Pollard, Bayonne, N.J., Assignors to General Dehydrator Co., New York. U.S. Pat. 1,138,380, May 4, 1915. Date of appl., Sept. 28, 1912. Renewed Oct. 14, 1914.

MILK at 37° C. (98° F.) is sprayed into dry air heated to 37° C. and the air carrying the milk in suspension is expanded and mixed with further quantities of dry air whilst passing through a chamber in which its temperature is maintained at about 37° C.—W. P. S.

*Milk and other liquids easily decomposed by heat; Sterilisation of* —. O. Lobeck, Ger. Pat. 282,027, Feb. 21, 1913.

THE milk or other liquid is first passed over a surface heated to above the sterilising temperature, and then kept in contact for the requisite time with a surface heated to the sterilising temperature. By thus heating the liquid suddenly to the requisite temperature sterilisation can be effected more rapidly and at a lower temperature than by the usual methods.—A. S.

*Meat products; Preparation of predigested* —. H. Watkins-Pitchford, Weybridge, Surrey, Eng. Pat. 19,087, Aug. 26, 1914. (See also Eng. Pat. 19,431 of 1912; (this J., 1913, 956).

LEAN minced meat is washed with warm water to remove salts and extractives, and digested with papaw fruit juice, papain, pepsin or other enzyme for 3 hrs. at 40° C. The mixture is then boiled for 30 mins., filtered, and the filtrate evaporated *in vacuo* to a syrup which is mixed with 20% of glycerin or other excipient. The product may be dried *in vacuo*. The fluid obtained may be combined with other food materials, such as cod liver oil, milk, wine, etc.—J. H. J.

*Organic substances; Process of conserving* —. H. Goslar, Aachen, Germany. U.S. Pat. 1,138,602, May 4, 1915. Date of appl., Aug. 6, 1914.

FLESH, blood, animal glands and juices, fruit juices, or vegetables are mixed with fibrin- and gluten-containing substances, and the mixture is moistened, and rolled into thin sheets, which are dried quickly at a low temperature.—W. P. S.

XIXB. - WATER PURIFICATION ;  
SANITATION.

*Water; Determination of dissolved oxygen in* —. L. W. Winkler. Z. anal. Chem., 1914, 53, 665-672.

THE following modification of the author's well-known method is described for the determination

of dissolved oxygen in water containing both nitrites and organic substances. A bottle is filled with the water, manganous chloride solution and sodium hydroxide solution (free from potassium iodide) are added in the usual way, and a current of carbon dioxide is then passed into the water. The manganous hydroxide is thus converted into manganous carbonate and bicarbonate; about 10 minutes' treatment with carbon dioxide is sufficient. The precipitate is collected on a filter, washed with 2% potassium bicarbonate solution, then dissolved in dilute hydrochloric acid containing potassium iodide, and the liberated iodine titrated with thio-sulphate solution. The manganous carbonate is not oxidised by atmospheric oxygen during the filtration.—W. P. S.

*Reducing power of natural waters; Determination of the* —. L. W. Winkler. Z. anal. Chem., 1914, 53, 561-564. J. Chem. Soc., 1915, 103, ii., 287-288.

THE following procedure is recommended for waters containing nitrites, ferrous salts, and manganese salts: 100 c.c. of the water is treated with 1 c.c. of 10% sodium hydroxide solution, and set aside for five minutes; ferrous and manganous salts are thus oxidised by the dissolved oxygen in the water. Ten c.c. of N/100 alkaline potassium permanganate solution is added, and after the lapse of twenty-four hours the mixture is acidified with 25% phosphoric acid solution (this is preferable to sulphuric acid as it prevents the action of the ferric salts on potassium iodide), potassium iodide is added, and the iodine titrated with thio-sulphate. Another portion of the water is also treated with sodium hydroxide solution to oxidise the ferrous and manganous salts, permanganate solution is then added, and the excess titrated after two minutes' contact. The nitrites are thus oxidised, whilst the organic matter is not appreciably attacked: the result is a measure of the substances, other than organic matters, which reduce permanganate.

*Sludge from town sewage; Value of* — as a source of fat. D. Halde, Seifensieder Zeit., 1914, 41, 1151-1153. Z. angew. Chem., 1915, 28, Ref., 13-14.

THE sludge is subjected to a preliminary treatment with acid and extracted with a solvent; the extracted sludge is pressed to remove the greater part of the water and, when mixed with one-fourth of its weight of coal, serves as a fuel, or it may be used directly as a fertiliser. The crude fat, separated from the solvent, is dark brown in colour; on distillation it yields a product consisting of about equal parts of stearine and oleine, about 20% of pitch remaining in the retort. The stearine, separated from the oleine by pressure, has m. pt. 45.3° C., and contains 6.4% of unsaponifiable substances; the dark brown oleine contains 19.4% of unsaponifiable substances.—W. P. S.

*Quassia as a contact insecticide*. W. B. Parker. Bull. U.S. Dept. Agric., No. 165. Dec. 31, 1914. 8 pages.

A solution of quassia containing 0.4 grm. in 2000 c.c. of water was found to be only slightly inferior to a 10% solution of nicotine sulphate in exterminating the hop aphid (*Phorodon humuli*, Schrank) and the prune aphid (*Hyalopterus pruni*, Fab.) in a moist district of California. The cost of the materials for 100 gallons of spray is given as 24 cents (1s.). E. H. T.

*Destruction of house-fly larvae in horse manure*. Cook and others. See XVI.



## PATENTS.

*Filters [; Sand —];* F. H. Desrumaux, Paris. Eng. Pat. 13,481, June 2, 1914.

In a sand filter which is cleaned by reversal of the current, the scraper for the filtering material is operated through reducing gear by a turbine in a central compartment, which can be worked either by the unfiltered water, or by the filtered water when the flow is reversed.—W. F. F.

*Detritus; Process for separating — from liquids.* J. M. Davidson, Assignor to W. B. Scaife and Sons Co., Pittsburgh, Pa. U.S. Pat. 1,138,634, May 11, 1915. Date of appl., Jan. 7, 1914.

The mixture is filtered through a bed of granular material, a current of air being passed upwards through the bed to prevent the choking of the surface by a layer of the detritus. When filtration is finished, the detritus on the surface is dried by reversing the current of air or by substituting a heated gas. Instead of air, a fluid lighter than the liquid being filtered may be passed upwards through the filter and subsequently passed downwards to dry the deposited cake; or for the latter purpose, a current of steam may be used.—J. H. J.

*Sewage or other wastes; Process of purifying — and apparatus therefor.* L. C. Frank, Washington, D.C. U.S. Pat. 1,139,021, May 11, 1915. Date of appl., April 2, 1915. (Dedicated to the public.)

The sewage is led down by a pipe to the bottom of the central chamber of a tank and flows upwards. Air is admitted, also at the bottom, and oxidises the sewage, which overflows at the top of the chamber into two V-shaped side chambers where settling takes place; the deposited solids fall through openings at the bottom of the side chambers into the central chamber, while the clear liquid passes to the effluent channel.—J. H. J.

*Sewage disposal; Apparatus for —.* J. M. Davidson, Assignor to W. B. Scaife and Sons Co., Pittsburgh, Pa. U.S. Pat. 1,139,402, May 11, 1915. Date of appl., Nov. 29, 1912. Renewed April 9, 1915.

A closed horizontal tank has a filtering layer of sand in its lower portion through which sewage is forced by pressure. The sludge collected on the surface is dried by forcing air through it, and is removed through manholes in the side of the tank at the sand level.—J. H. J.

*Waters, liquids, and sewage; Electrochemical process of treating —.* C. P. Landroth, Philadelphia, Pa. U.S. Pat. 1,139,778, May 18, 1915. Date of appl., Oct. 12, 1911.

The putrescent liquid is treated with sufficient calcium hydroxide to render it distinctly alkaline and to produce a flocculent precipitate. An electric current is passed through the mixture, producing nascent oxygen, which acts on the putrescent material, so that a non-putrescent effluent charged with oxygen is obtained.—J. H. J.

*Water; Method of treating — [and utilising slag].* W. H. Williams, Sharpsburg, Pa. U.S. Pat. 1,139,618, May 18, 1915. Date of appl., May 4, 1914.

MOLTEN slag is run into the water in a tank and is disintegrated, whilst certain of the mineral constituents dissolve in the water. The solution is drawn off from time to time and used for industrial purposes, the tank being supplied with more water.—J. H. J.

*Water-purifying apparatus.* H. B. Hartman, Assignor to Electric Water Sterilizer Co., Scottsdale, Pa. U.S. Pats. (A) 1,139,969 and (B) 1,139,970, May 18, 1915. Dates of appl., Aug. 12, 1913, and June 11, 1914.

(A) THE apparatus comprises a coagulation

chamber and a filter chamber, containing a filter bed with a screen above the material, which is washed by reversing the flow of water. (B) The water is first electrolysed and then passed through the coagulation and filter chambers. The precipitate produced in the electrolysing chamber is mixed with water from the coagulation chamber and is then passed to the filter bed.—J. H. J.

*Animal-dip; Preparation of a concentrated —.* R. M. Chapin, Washington, D.C. U.S. Pat. 1,137,844, May 4, 1915. Date of appl., May 28, 1914. (Dedicated to the public.)

TEN lb. of arsenious oxide is dissolved in a solution of 4 lb. of caustic soda in one gallon of water, the mixture being stirred continuously, whereby the temperature is maintained at near the boiling point; 10 lb. of crystallised sodium carbonate is added and the mixture diluted to 5 gallons. This concentrated solution may be diluted to an appropriate extent. There is then added to it a mixture of 0.5 lb. of caustic soda, 1 quart of water, and 1 gallon of pine tar.—J. H. J.

## XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.

*Pareira root; Alkaloids of the —.* M. Scholtz and O. Koch, Arch. Pharm., 1914, 252, 513–530. Z. angew. Chem., 1915, 28, Ref., 163.

PAIREIRA root contains mainly bebeerine, or sometimes  $\beta$ -bebeerine, Bebeerine, isobeeberine, and  $\beta$ -bebeerine are isomeric compounds. Iso-bebeerine is an isoquinoline derivative and an isomeride of codeine. As the free hydroxyl group is phenolic in character, isobeeberine resembles morphine in its behaviour towards several reagents. Isobeeberine is not a febrifuge, but is a narcotic. — F. W. A.

*Kombé strophanthin.* D. H. Brauns and O. E. Closson, Arch. Pharm., 1914, 252, 291–341. Chem.-Zeit., 1915, 39, Rep., 131.

GENUINE Kombé strophanthin seeds contain a crystalline, glucoside strophanthin,  $C_{40}H_{56}O_{12} \cdot 3H_2O$ , and a closely related amorphous strophanthin of probably double the molecular weight. The former is converted by water into an amorphous, monobasic, acid derivative, which, like both strophanthins, is hydrolysed to strophanthidin,  $C_{20}H_{28}O_6 \cdot H_2O$ , m. pt. 169–170°C., by dilute acids. Crystalline Kombé strophanthin does not contain a pentose or a rhamnose, but yields a disaccharide and methyl alcohol on acid hydrolysis. Amorphous strophanthin appears, however, to contain a pentose. The crystalline strophanthin and its acid derivative act as heart tonics; the latter having the weaker effect. — T. C.

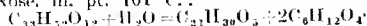
*Harmine and harmaline; Therapeutic value of —.* Chem. and Drug., June 5, 1915.

EXPERIMENTS on prisoners in Lahore Central Jail have shown that harmine and harmaline (from the seeds of *Peganum Harmala*, L.) are not so effective as quinine in the treatment of malaria, and further they produce nausea and giddiness. (Compare this J., 1915, 570.)

*Anhydrogitalin and a by-product of the manufacture of digiloxin.* H. Kiliani, Ber., 1915, 48, 331–349. J. Chem. Soc., 1915, 108, i., 281–282. (See also this J., 1914, 210, 1071.)

ANHYDROGITALIN is prepared by the addition of ether to a solution of gitalin in methyl alcohol and chloroform (equal volumes). It has m. pt. 255°, after sintering at 250°C. Analyses agree with

the formula  $C_{33}H_{52}O_{12}$ , instead of  $C_{28}H_{44}O_8$ , given by Kraft (this J., 1911, 709). Hydrolysis with acid (100 (ac. 50% alcohol + 1 c.c. concentrated hydrochloric acid) yields anhydrodigitaligenin, m. pt. 200° C. (216°—219° C. according to Kraft), and digitoxose, m. pt. 101° C.:



The sparingly soluble by-products of the manufacture of digitoxin were contaminated with some coloured impurity which could not be removed in a practical manner. The mass was therefore extracted with methyl alcohol, and, without further purification, hydrolysed in the same manner as anhydrodigitalin. Digitoxose, m. pt. 101° C. [α]<sub>D</sub> = +45.6°, was thereby obtained, and a substance,  $C_{22}H_{32}O_6$ , shining leaflets, m. pt. 205—206° C. The latter gives a dibenzoyl derivative, and is dissolved by sodium hydroxide, yielding a sodium salt from which hydrochloric acid regenerates an isomeric compound,  $C_{22}H_{32}O_6$ .

Oxidation of digitoxose with nitric acid of sp. gr. 1.2 under definite conditions and treatment of the product with calcium carbonate yields calcium tartrate, calcium digitoxonate, and calcium dihydroxyglutarate.

The parent glucoside, which forms the chief constituent of the sparingly soluble by-product, was obtained as a perfectly white precipitate, m. pt. 190° C., by treatment with methyl alcohol-chloroform-ether; analyses agree only approximately with the formula,  $C_{24}H_{32}O_{12}$ .

*Chrysarobin; Commercial*.—J. R. Eder, Arch. Pharm., 1915, 253, 1—33. Z. angew. Chem., 1915, 28, Ref. 189. (See also this J., 1912, 253; 1913, 1126.)

COMMERCIAL chrysarobin after oxidation by air in alkaline solution was found to consist of about 26% of amorphous dark violet and brownish red products, 18% of dehydro-emodinanthranol monomethyl ether, 2% of emodin, and 32% of a mixture composed of 71% of chrysophanic acid and 29% of emodin monomethyl ether. Dehydro-emodinanthranol monomethyl ether is also present in the original chrysarobin, which contains, in addition, chrysophanic acid, emodin monomethyl ether, and emodin, either wholly or partly in a reduced form. The presence of dichrysarobin methyl ether, mentioned by Jowett and Potter (Chem. Soc. Trans., 1902, 81, 1577) is considered very improbable. A. S.

*Siamese gum benzoin; A new crystalline constituent of*.—F. Reinitzer, Arch. Pharm., 1911, 252, 311. Chem.-Zeit., 1915, 39, Rep. 139.

SIAMESE gum benzoin, according to Lidy (this J., 1894, 821), consists mainly of a mixture of two benzoic esters, the alcohols being benzoinol,  $C_{15}H_{14}O_2$ , and siamesinotannol,  $C_{17}H_{16}O_3$ . A new colourless crystalline benzoate of a previously unknown resin-alcohol, for which the name lubanol is proposed, has been isolated. J. R.

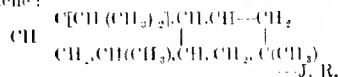
*Citronella oil; A new oxide in Java*.—K. E. Spornitz, Ber., 1911, 47, 2178—2182. Bull. Soc. Chim., 1915, 18, 250—251.

THE high-boiling fractions (190—200° C. at 15 mm. pressure) of Java citronella oil, which contain a substance,  $C_{20}H_{30}O$ , yield dicitronelloxide when redistilled from sodium. This yields tetrahydrodicitronelloxide on reduction and when treated with dry hydrogen chloride in ethereal solution yields a hydrochloride, m. pt. 107.5° C. The latter, on boiling with alcoholic potassium hydroxide, changes to isodicitronelloxide, isomeric with the former oxide. Semmler and Jonas (this J., 1913, 745) appear to have obtained the optical antipode of the above dicitronelloxide by heating citronellol with anhydrous oxalic acid in a sealed tube.—J. R.

*Copaene, and a new class of tricyclic sesquiterpenes.*

F. W. Semmler and H. Stenzel, Ber., 1911, 47, 2555—2561. Bull. Soc. Chim., 1915, 18, 251—252.

THE volatile essential oil of the African copaiba tree contains a *d*-rotatory sesquiterpene (the dihydrochloride of which yields *t*-cadinene), small quantities of  $\beta$ -caryophyllene, and a sesquiterpene named copaene. The last-named boils at 119°—120° C. under 10 mm. pressure, and gives a hydrochloride melting at 117°—118° C., which upon losing hydrochloric acid furnishes cadinene. Copaene yields dihydrocopaene on reduction; the two substances appear to be derived from tricyclic naphthalene. When ozonised in acetic acid copaene yields copaneketic acid,  $C_{15}H_{22}CO_2$ , which is oxidised by permanganate to a glycol,  $C_{12}H_{20}O_2$ . The following structure is suggested for copaene:



*Antipyrine; Transformation of—into diantipyrinemethane by formaldehyde.* [Detection of antipyrine in pyrimidine.] C. Astre, Bull. Soc. Chim., 1915, 17, 175—179.

ANTIPYRINE is rapidly transformed into diantipyrinemethane at about 90° C. by formaldehyde in presence of water, but a trace of alkali is sufficient to hinder the reaction and render it incomplete. Vessels of platinum or of glass previously well washed with boiling hydrochloric acid should therefore be used in the operation. Pyrimidone (dimethylaminoantipyrine) inhibits the reaction completely unless carefully neutralised with acid. Antipyrine is detected and estimated in pyrimidone by dissolving 1 gm. in 5 c.c. of water on the water-bath and neutralising with formic acid in presence of methyl orange; 1 c.c. of formaldehyde is added, and the mixture warmed for 1½ hours on the water-bath. After standing for 12 hours the yield of diantipyrinemethane crystals is approximately 0.09 gm. per 0.1 gm. of antipyrine in the original pyrimidone.—J. R.

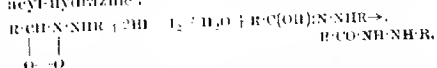
*Phenylurethane derivatives as local anaesthetics.* K. Fromherz, Arch. exp. Path. u. Pharm., 1911, 76, 257. Chem.-Zeit., 1915, 39, Rep. 161.

THE introduction of a methane or phenylurethane grouping into a substance has little influence on its action as a local anaesthetic. —E. C.

*Hydrazones; Autooxidation of*.—M. Busch and W. Dietz, Ber., 1911, 47, 3277—3291. J. Chem. Soc., 1915, 108, i, 307—308.

WHEN solutions of aldehydephenylhydrazones in hydrocarbons are exposed to air and light, the primary product is a peroxide, which, under suitable circumstances, can be readily isolated. These peroxides are relatively stable in solution, but, when dry, are generally highly unstable, frequently exploding after a short time without apparent reason. Benzaldehyde-*p*-bromophenylhydrazone in this respect forms a marked exception. Water does not appear to have a marked effect on the autooxidation of hydrazones.

The hydrazone peroxides readily give up one atom of oxygen, and can thus be estimated iodometrically, one half of the oxygen being used in oxidising the hydroiodic acid, whilst the other remains in the molecule, forming the corresponding acyl-hydrazine:



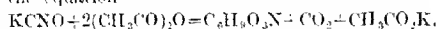
The hydrazone peroxides are very susceptible to the action of hydrogen and hydroxyl ions. In the

former case an acylhydrazine is first formed, which is partly oxidised by the available oxygen atom of the unchanged peroxide to the corresponding azo-compound; in the latter case, larger quantities of other products are formed.

The preparation of the peroxides is generally effected by the action of oxygen under slight pressure on a solution or suspension of the hydrazine in benzene or petroleum.

*Secondary amides: New method for the preparation of —.* K. Brunner, Ber., 1914, 47, 2671—2680. J. Chem. Soc., 1915, 108, i., 224—225.

POTASSIUM CYANATE reacts with acetic anhydride diluted with benzene or ether, in accordance with the equation



The nitrogen compound (probable constitution  $\text{CH}_3\text{CO}_2\text{OC}(\text{CH}_3)_2\text{NCOCH}_3$ ) is a colourless liquid, b. pt.  $86^\circ\text{--}90^\circ\text{C}$ . at 11 mm., solidifying to rectangular leaflets, m. pt.  $7^\circ\text{--}8^\circ\text{C}$ .; when heated under ordinary pressure it yields diacetamide and a carbonaceous residue. Diacetamide is also produced when the new substance is exposed to the atmosphere for a short time, and in the absence of special precautions, diacetamide is the usual product of the interaction of potassium cyanate and acetic anhydride. Good yields of secondary amides can be obtained in a similar way from propionic, butyric, and isobutyric anhydrides, but with benzoic anhydride the yield of dibenzamide is very poor, small quantities of tribenzamide and benzonitrile also being obtained. Potassium thiocyanate exhibits similar behaviour to the cyanate towards acetic anhydride, giving diacetamide. Semicarbazide hydrochloride is a convenient reagent for distinguishing secondary from primary amides. With the latter class of compound no appreciable change is obtained in aqueous solution with this substance to which a little potassium acetate has been added, whereas diacetamide under these conditions gives a deposit of hydrazoformamide.

*Methylenediamine.* P. Knudsen, Ber., 1914, 47, 2698—2701. J. Chem. Soc., 1915, 108, i., 220.

DIFORMOMETHYLENEDIAMIDE,  $\text{CH}_2(\text{NH}\cdot\text{COH})_2$ , was prepared by heating together 60 grms. of trioxymethylene and 180 grms. of formamide for 4—5 hours under a reflux condenser; yield, 77 grms. Hydrolysis of this by concentrated hydrochloric acid gave rise to 57 grms. of methylenediamine dihydrochloride, colourless, hygroscopic prisms. By hydrolysis with nitric acid, the nitrate was obtained in prismatic crystals which on heating melt and then explode; the sulphate, small crystals, was obtained by hydrolysis with sulphuric acid of 50% concentration. It was not found possible to isolate the free base; solutions in such solvents as alcohol are fairly stable and have an ammoniacal odour. The hydrochloride decomposes rapidly in aqueous solution, producing formaldehyde; when heated with formaldehyde solution the hydrochloride reacts, forming methylamine hydrochloride and carbon dioxide.

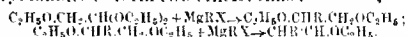
*Formaldehyde and ammonia: The Pöchl reaction between —.* P. Knudsen, Ber., 1914, 47, 2691—2698. J. Chem. Soc., 1915, 108, i., 220—221.

THE reaction between formaldehyde and ammonia or amines discovered by Pöchl, which has been used for the preparation of trimethylamine (Eschweiler, Berichte, 1905, 38, 889; Koeppe, Ber., 1905, 38, 882) and of methylamine (Brochet and Cambier, Comptes rend., 1895, 120, 449), can be applied also to the preparation of dimethylamine by distillation of a solution of ammonium

chloride in a sufficient excess of formaldehyde solution under ordinary pressure: the distillate from 100 grms. of ammonium chloride and 1 kilo. of 40% formaldehyde solution contained 5.7 grms. of ammonium chloride with 11.3, 66.1, and 44.4 grms. respectively of the hydrochlorides of methylamine, dimethylamine, and trimethylamine.

*Aldehydes: New syntheses of —.* I. E. Späth, Monats. Chem., 1915, 36, 1—12. J. Chem. Soc., 1915, 108, i., 262—263.

ETHOXYACETAL reacts with magnesium alkyl or aryl halides to form two ethers, thus:



These ethers are readily hydrolysed to the same aldehyde, and the method offers a convenient synthesis even of sensitive aldehydes. Several substituted phenylacetaldehydes are described; they all possess fragrant odours. Ethoxyacetal, b. pt.  $57^\circ\text{--}58^\circ\text{C}$ . at 11 mm., was prepared from bromoacetal (Fremmler and Ledru, Comptes rend., 1905, 140, 794) by heating it with a cold concentrated solution of sodium ethoxide, and was purified by boiling with sodium. The aldehydes were prepared by adding ethoxyacetal to the Grignard reagent, heating the mixture under a reflux condenser (allowing the solvent ether to escape), decomposing the product by dilute hydrochloric or acetic acid, isolating and distilling the mixed ethers, and allowing these to drop into boiling, about 50% sulphuric acid at such a rate that the product distilled over in the steam. The aldehydes were isolated from the ethereal extract of this distillate by means of sodium bisulphite, and the unchanged ethers submitted to hydrolysis again.

Attempts were also made to prepare chlorohydrins by the interaction of chloroacetaldehyde with magnesium alkyl or aryl halides and to convert these into glycol ethers and then into aldehydes, but in most cases ethylene oxides were obtained.

*Tautomeric, isomeric, and polymeric substances: Method of distinguishing — from polymorphic substances.* N. V. Skidwick, Chem. Soc. Trans., 1915, 107, 672—678.

WHEN a substance occurs in several modifications this may be due either to a difference in the structure of the molecules (tautomerism, dynamic isomerism, or polymerism) or in the arrangement of the molecules in the crystal (polymorphism). In the latter case the difference disappears when the substances are dissolved or vaporised. If a substance occurs in two forms and a quantity of the less soluble form be added to a saturated solution of the more soluble form, the total concentration will not increase, but may possibly diminish, if the substances are polymorphic, whereas if the two forms are tautomeric, the less soluble form will dissolve in the solution, irrespective of the presence of the more soluble form (unless the tautomeric change is very rapid), and the concentration will increase. The change in concentration is readily ascertained by determining the freezing point of the pure solvent, adding successively small quantities of the finely powdered, more soluble modification until the solution is saturated, shown by the freezing point remaining constant, and then adding successive small quantities of the finely powdered, less soluble form until the freezing point is again constant. A lowering of the freezing point on the addition of the less soluble form (corresponding to an increase of concentration) indicates that the two forms are tautomeric or isomeric. If only a small depression of the freezing point is obtained on the addition of the less soluble modification, the depression given by this alone

in the pure solvent should be determined. By this method, using benzene as the solvent, it was found that the two phthalylphenylhydrazides, m. pt. 184° C., are polymorphic, whilst the third form, m. pt. 216° C., is isomeric or tautomeric; the two phthalylphenylmethylhydrazides, white and yellow, the two forms (needles and stout prisms) of *p*-bromoacetanilide and 2,4-dibromoacetanilide, the yellow *p*-nitrophenol insensitive to light and the yellow form sensitive to light, are in each case polymorphic, whilst the keto and enol forms of benzoylcamphor and the dextro and levo forms of camphoric anhydride behave as tautomeric or isomeric compounds.—T. C.

*Ethyl acetate: Analysis of*——. P. Szeberényi. Z. anal. Chem., 1914, 53, 683. J. Chem. Soc., 1915, 108, ii., 292–293.

THE ester-content is found by saponification. A quantity of 25 grms. of the acetate is then saponified with aqueous alkali solution, distilled, and the alcohol estimated in the distillate; the quantity of alcohol thus found represents that present both in the combined and free state in the sample, and the amount of free alcohol is calculated. The quantity of water present in the sample is found by difference. The total amount of alcohol may also be found by oxidising the sample directly with potassium bichromate solution in the presence of sulphuric acid. One c.c. of N/2-potassium bichromate solution corresponds with 5.7625 mgrm. of ethyl alcohol. In this estimation the combined alcohol is oxidised as well as the free alcohol, if the latter is present, whilst the acetic acid liberated is not attacked.

*Salicylates of lead and copper.* W. O. de Couinek. Bull. Soc. Chim., 1915, 17, 163–164.

NORMAL lead salicylate dihydrate was obtained by gradually dissolving lead carbonate in an aqueous solution of the acid at 70° C. and cooling slowly. Mixtures of basic salts from which no homogeneous salt could be isolated resulted when the above salt was warmed with ammonia under varying conditions. Normal cupric salicylate dihydrate was prepared by mixing strong aqueous solutions of normal calcium salicylate and copper sulphate, adding alcohol, and cooling rapidly; it is readily resolved into basic salt and free acid when warmed with water, alcohol, or ether. The normal salicylates of divalent metals are considered to be molecular complexes of the basic salts with salicylic acid; the less stable members are decomposed in the manner exemplified by the cupric salt, while the more stable members are resolved at the temperature of decomposition of salicylic acid into basic salt, phenol, and carbon dioxide.—J. R.

*Mercurial powder.* P. G. Unna. Dermatol. Wochensh., 1915, 337. Chem. and Drugs, 1915, 86, 50.

WHEN mercury is triturated with turpentine oil and lycopodium, a dry, uniform, yellowish-grey powder is obtained almost immediately, in which the mercury remains completely divided. A powder containing 33% of mercury can be prepared in this way. The product can be worked up readily into mercurial ointment and plasters.

*Citral in concentrated oil of lemon: Determination of*——. E. Böcker. J. prakt. Chem., 1914, [iii], 90, 393–404. J. Chem. Soc., 1915, 108, ii., 294.

CONCENTRATED oil of lemon is adulterated principally by addition of citral derived from lemon-grass oil. Such addition does not increase the content of volatile, oxygenated compounds, on which the value of the oil as a perfume depends. The citral-content of these oils may be determined

with a considerable degree of accuracy by the sodium sulphite method devised by Burgess (this J., 1901, 1178); methods in which sodium bisulphite is used give erroneous results. The proportion of citral present is not sufficient to indicate addition of citral, but, taken in conjunction with the hydrocarbon-content of the oil (compare this J., 1914, 275), it will show if the proportion added is large. The highest percentage of citral found in oil of lemon free from terpenes and sesquiterpenes is 66, the content varying inversely with the hydrocarbons present. Consequently, if an oil of lemon contains either no hydrocarbons and more than 66% of citral, or 50% of hydrocarbons and more than 33% of citral, addition of the latter must have occurred. Since, however, the genuine hydrocarbon-free oil usually contains less than 66% of citral, the above method gives no more than the minimal value of the adulteration, and may, unless the latter amounts to about 20%, not detect it at all.

*Vanillin: Reactions of*——. E. P. Häussler. Z. anal. Chem., 1914, 53, 691–695. J. Chem. Soc., 1915, 108, ii., 294. (Compare this J., 1914, 612; 1915, 573.)

WHEN albumin, casein, peptone, or fibrin is treated with a small quantity of dilute alcohol and evaporated with the addition of vanillin, a yellow coloration is obtained which changes to violet when treated with hydrochloric acid and again evaporated. Blue or violet colorations are obtained by subsequent treatment with ammonia and then with hydrochloric acid. Urea yields a yellow coloration when evaporated with vanillin and the residue treated with hydrochloric acid, and a red coloration after treatment with ammonia and hydrochloric acid. The colorations obtained under similar conditions with gelatin are brown.

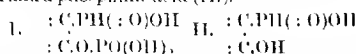
*Unsaturated compounds: Behaviour of*—— towards phosphorus and oxygen. Oxidation catalysis. II. R. Willstätter and E. Sonnenfeld. Ber., 1914, 47, 2801–2811. J. Chem. Soc., 1915, 108, i., 326–328.

IT has been shown previously (J. Chem. Soc., 1913, 104, i., 1200) that osmium facilitates the oxidation of unsaturated compounds by gaseous oxygen, and colloidal osmium has now been found to be much more effective than the ordinary powder. The behaviour of phosphorus is essentially different from that of osmium, in that the phosphorus enters into the composition of the product. In the experiments with phosphorus, this element was used in a finely divided condition, obtained by shaking with warm water and then cooling; benzene, light petroleum, and cyclohexane were used as solvents. The formation of the new phosphorus compounds can be easily observed by introducing the phosphorus together with a solution of the olefine into a test-tube and allowing access of air through a calcium chloride tube, when colourless needles appear in a few hours. Analysis of the products, together with measurements of the ratio, oxygen absorbed: olefine consumed: phosphorus consumed, prove the addition of the grouping  $P_2O_4$  at the double bond. By checking the absorption at an intermediate point, products containing the added group  $P_2O_4$  can be obtained. These two classes of compounds, from their analogy in composition to the nitrosites and nitrosates of the terpenes, are termed phosphorites and phosphorates, and their behaviour suggests the structures



respectively. The phosphorates are very hygroscopic, colourless or pale yellow solids, vigorously

decomposed by water, giving an ester acid (I.) which further undergoes hydrolysis into phosphoric acid and a phosphinic acid (II.).



The decomposition of the phosphorates by water is so vigorous that flame may ensue, due to the formation of phosphine from the phosphinic acid, and to this source is also due the phosphine odour observable with the phosphorates and still more with the phosphorites.

Cyclohexene phosphorate,  $\text{C}_6\text{H}_{10}\text{P}_2\text{O}_4$ , is a hygroscopic, pale yellow, crystalline powder with an odour of phosphine due to the action of moisture; when heated it decomposes generally near 160° C. Menthe phosphorate,  $\text{C}_{10}\text{H}_{16}\text{P}_2\text{O}_4$ , yellowish-white powder, pinene phosphorate,  $\text{C}_{15}\text{H}_{24}\text{P}_2\text{O}_4$ , and trimethylcyclohexene phosphorate were also prepared. Allyl alcohol behaved exceptionally, yielding a colourless, crystalline substance of the composition,  $(\text{C}_3\text{H}_5\text{O})_3\text{P}_2\text{O}_4$ . Unsaturated acids and esters also yield phosphorates; thus, oleic acid gave an amorphous phosphorate,  $\text{C}_{17}\text{H}_{31}\text{O}_7\text{P}_2\text{O}_4$ , olive oil gave an amber-like resin, whilst poppy oil produced a gelatinous compound.

The inhibitive effect of ethylenic compounds on the luminous oxidation of phosphorus, attributed by Schönbein to their effect on the ozone which acts as a positive catalyst, is explained by the authors as due to the formation of a thin film of resinous substances arising from the action of moisture on the primarily formed phosphorate. Attention is drawn to the formation of phosphorates in the so-called "phosphorated oils," such as a solution of phosphorus in olive oil, and their possible influence on the medicinal properties.

*Arsenic: New method for the introduction of into organic compounds.* G. Roeder and N. Blaschke, Ber., 1914, 47, 2748—2752. J. Chem. Soc., 1915, 108, i, 331.

CONTRARY to the observation of Michaelis (Annalen, 1902, 320, 271; 321, 141), the chloromercuric compounds of the type  $\text{R.HgCl}$ , easily derivable from unsaturated substances in many cases, supply an easy method of producing organic dichloro-arsines by the reaction  $\text{R.HgCl} + \text{AsCl}_3 = \text{HgCl}_2 + \text{RAsCl}_2$ . Such groups as the carboxyl, hydroxyl, and amino-radicals which react with arsenic trichloride must be suitably protected in order to avoid the formation of hydrogen chloride, and the method is also limited by mercurization of a substituted benzene generally yielding only ortho- and para-compounds, of which the latter are alone capable of reacting readily with the arsenic trichloride. This characteristic difference between the substituent chloromercuric groups in the ortho- and para-positions renders possible the production of a new class of compound containing both mercury and arsenic, the therapeutic value of which may be considerable. The following are given as examples. A mixture of 100 c.c. of pure benzene with 50 c.c. of an acetic acid solution of mercuric acetate was heated in a closed flask in boiling water for five hours. The benzene filtrate and washings were evaporated to a small bulk and treated with an alcoholic solution of calcium chloride, when chloromercuric benzene separated. When 30 grms. of chloromercuric benzene was heated on the water-bath with 100 grms. of arsenic trichloride for four to five hours, crystals of mercuric chloride separated, and the supernatant liquid on distillation yielded phenyldichloroarsine,  $\text{C}_6\text{H}_5\text{AsCl}_2$ , b. pt. 250—255° C., a pungent liquid which could be converted by the action of chlorine and water into phenylarsinic acid, m. pt. 158° C. Bromomercuric benzene and iodomercuric benzene were

also prepared in a similar manner, and reacted satisfactorily, as also did the acetoxymercuric compound, with arsenic trichloride. By interaction of chloromercuric anisole with arsenic trichloride in the same proportions and under the same conditions as for the corresponding benzene compound, anisoyldichloroarsine was obtained and was further converted into anisylarsinic acid m. pt. 179°—180° C.

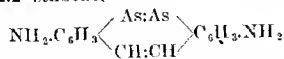
*Arsenic acids: Secondary aliphatic-aromatic—and their reduction products, especially 3,3'-diamino-4,4'-dihydroxydiphenyldimethylhydriarsine.* A. Berthelm, Ber., 1915, 48, 350—359. J. Chem. Soc., 1915, 108, i, 331—332.

THE reaction of alkyl halides with aromatic arsenic oxides in the presence of alkali (compare Ehrlich and Berthelm, Berichte, 1910, 43, 917) leading to the formation of alkyl-aryl-arsinic acids, has been found to be of general application. Iodides are more reactive than chlorides but the hydriodic acid formed interferes with the isolation of the arsenic acid and must be removed either by precipitation with silver nitrate followed by precipitation of the silver salt of the arsenic acid, or by treatment of the reaction mixture with freshly precipitated silver chloride. The secondary arsenic acids are well crystallised substances, which, like cacodylic acid, have an amphoteric character; they are extraordinarily resistant to oxidation by nitric acid. 3,3'-Diamino-4,4'-dihydroxydiphenyldimethylhydriarsine,  $\text{As}_2(\text{CH}_3)_2[\text{C}_6\text{H}_3(\text{OH})_2\text{NH}_2]_2$ , is colourless and forms crystalline salts; its toxicity is greater and its therapeutic action less, than that of salvarsan. Phenylmethylarsinic acid,  $(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{AsO}_2\text{OH}$ , white, silky needles, m. pt. 179.5° C. after previous softening, is prepared by the action of methyl iodide on a solution of phenylarsine oxide in alcohol and 10N-sodium hydroxide, and is purified through the silver salt  $\text{C}_6\text{H}_5\text{O}_2\text{AsAg}$ . Its aqueous solution is acid to litmus, but not to methyl orange. It yields a hydrochloride and a crystalline nitrate. Phenylethylarsinic acid crystallises in colourless, four-sided prisms combined with pyramids, m. pt. 108° C. (after previous softening) when rapidly heated. Phenylisopropylarsinic acid, prisms, melts at 108° C. after previous softening. *p*-Amino-phenylmethylarsinic acid is a crystalline powder, m. pt. 201° C. after previous softening. The corresponding acetyl derivative is prepared from *p*-acetylaminophenylarsine oxide, and forms needles, m. pt. 260° C. (decomp.) after previous softening. Phenylbenzylarsinic acid, shining needles, m. pt. 206—207° C. after previous softening, is decomposed by hot concentrated hydrochloric acid into benzyl chloride and phenylarsine oxide or diiodide. 3-Nitro-4-hydroxy-phenylmethylarsinic acid melts at 232—233° C. (decomp.). Sodium hydrosulphite reduces it to the amino-derivative, needles, m. pt. 206—207° C. (decomp.) after previous darkening, and this when treated with hypophosphorous acid of sp. gr. 1.136 and hydriodic acid of sp. gr. 1.7, yields the hypophosphite of 3,3'-diamino-4,4'-dihydroxydiphenyldimethylhydriarsine.

*Stilbene-arsinic acids and their derivatives. Aromatic arsenic compounds.* I.A. P. Karrer, Ber., 1915, 48, 305—315. J. Chem. Soc., 1915, 108, i, 333—334.

THE author has prepared a number of arsenic stilbene derivatives in which the phenyl radicals are joined by two bridges. 5-Nitro-2-methyl-phenylarsinic acid is transformed by moderately concentrated sodium hydroxide into dyes of the type of Mikado brown, which on reduction form

alkaline solution yield 5,5'-diamino-2,2'-stilbene-diarsinic acid, from which 5,5'-diamino-1,1'-arseno-2,2'-stilbene,



is obtained by means of hydrosulphite. 5,5'-Diamino-4,4'-dihydroxy-1,1'-arseno-2,2'-stilbene is obtained by condensation of 4-chloro-5-nitro-*o*-tolylarsinic acid to 4,4'-dichloro-5,5'-dinitro-2,2'-stilbenediarsinic acid. The chlorine of the latter is replaced by hydroxyl by the action of concentrated sodium hydroxide, and the resulting compound reduced to the required stilbene derivative. The physiological properties of the substances are disappointing. *o*-Tolylarsinic acid, needles, m. pt. 160° C., is best prepared by the addition of sodium arsenite to a diazotised solution of *o*-toluidine, removal of excess of arsenic by hydrogen peroxide, and purification by means of the magnesium salt. It is converted by a mixture of concentrated sulphuric acid and nitric acid of sp. gr. 1.49 into 5-nitro-*o*-tolylarsinic acid, needles, which darken at 230° and melt at 261° C. The latter is converted by sodium hydroxide into a complex mixture of dinitro-*o*-, azoxy-, and azo-stilbenediarsinic acids, which is transformed by treatment with sodium hydroxide and zinc dust into sodium 5,5'-diamino-2,2'-stilbenediarsinate,  $\text{C}_{14}\text{H}_{11}\text{O}_6\text{N}_2\text{As}_2\text{Na}_2\cdot\text{H}_2\text{O}$ , from which the corresponding acid is readily obtained. Energetic reduction of the latter gives 5,5'-diamino-1,1'-arseno-2,2'-stilbene. 5,5'-Dinitro-2,2'-stilbenediarsinic acid is obtained by oxidation of the corresponding phenylarsinic acid by sodium hypochlorite and forms white crystals. 3,5-Dinitro-1-hydroxy-*o*-tolylarsinic acid, yellow needles, is prepared by nitration of 4-hydroxy-*o*-tolylarsinic acid; with concentrated sodium hydroxide solution it gives a stilbene dye, 4-chloro-*o*-tolylarsinic acid, needles, m. pt. 199° C. after softening at 195° C., is formed by the addition of sodium arsenite to a diazotised solution of *p*-chloro-*o*-toluidine, and is nitrated by concentrated sulphuric and nitric acids at 30°–10° C. to 4-chloro-5-nitro-*o*-tolylarsinic acid, leaflets, m. pt. 215° C. The latter yields a stilbene dye when treated with sodium hydroxide, in which, however, the chlorine atom is still present. 4,4'-Dichloro-5,5'-dinitro-2,2'-stilbenediarsinic acid, white, crystalline powder, is obtained by the action of sodium hypochlorite on an alkaline solution of 4-chloro-5-nitro-*o*-tolylarsinic acid, and is converted by further treatment with sodium hypochlorite and sodium hydroxide into 5,5'-dinitro-4,4'-dihydroxy-2,2'-stilbenediarsinic acid, from which, by reduction, 5,5'-diamino-1,1'-dihydroxy-4,4'-arseno-2,2'-stilbene is isolated.

*Esters of silicic acid.* G. Pellini. *Gaz. Chim. Ital.*, 1915, 45, 1, 380–385.

By the interaction of suitable proportions of *t*-bornoil and silicon tetrachloride dissolved in petroleum spirit, the author obtained tetra-*t*-bornyl silicate,  $(\text{C}_{10}\text{H}_{17}\text{O})_4\text{Si}$ , tri-*t*-bornyl monochlorosilicic ester,  $(\text{C}_{10}\text{H}_{17}\text{O})_3\text{SiCl}$ , di-*t*-bornyl dichlorosilicic ester, and mono-*t*-bornyl trichlorosilicic ester. The first two are crystalline solids, melting at 291°–292° and 215°–218° C. respectively, and easily soluble in petroleum spirit, benzene, and toluene. The dichloro compound is solid below 20° C. and boils at 263°–265° C. at 10 mm. pressure. The trichloro-compound boils at 110°–112° C. at 760 mm., and when dissolved in anhydrous ether and heated with silver oxide, is converted into the normal *t*-bornyl ester of dimetasilicic acid,  $(\text{C}_{10}\text{H}_{17}\text{O})_2\text{SiO}_2$ ; this separates from ether in glassy scales which soften at about 92° C. but have no definite melting point.—A. S.

*Colloidal medicinal substances.* T. Paul. *Münchener Pharm. Ges.*, June 24, 1914. *Chem.-Zeit.*, 1914, 38, 1050.

The objectionable taste of iron salts is a property of the ferrous and ferric ions and hence is missing in colloidal iron preparations. In aluminium acetate and acetotartrate solutions most of the aluminium is present in the form of colloidal basic salt and probably, also, of colloidal hydroxide; hence the astringent action due to aluminium ions is relatively feeble and the solutions do not cause irritation when applied to wounds. So-called colloidal silver preparations always contain substances which in aqueous solution lead to the formation of silver ions, and it is probable that the therapeutic action of the preparations is due to these ions. The quantity of silver ions, though small, is sufficient, for example, to saturate blood, owing to the relatively high concentration of chlorine ions therein. In some silver preparations, *e.g.*, protargol, the concentration of silver ions decreases with decreasing concentration of the preparation; in others, *e.g.*, sophol, it remains approximately constant; and in others, *e.g.*, argentanin, lysargin, collargol, and silver-ammonia compounds, it increases. A. S.

*Adsorption [of dyes, alkaloid salts, etc.] from aqueous solution.* Freundlich and Poser. See XI.

*Oil and amygdalin content of seed kernels of Prunus domestica.* Kassner and Beckmann. See XII.

*Oil of strophanthus seeds.* Matthes and Rath. See XII.

*Unsaturation constituents of strophanthus seed oil.* Heiduschka and Wallengruter. See XII.

*Organic acids from the sap of the sugar maple.* von Lippmann. See XVII.

*Origin of methyl alcohol in brandies.* [Methoxy-groups in cellulosic drugs.] Von Fellenberg. See XVIII.

*Chemical detection of blood.* Ganassini. See XXIII.

*Determination of the non-protein nitrogen in blood.* Greenwail. See XXIII.

#### PATENTS.

*Quinoline compounds, and process of producing the same.* A. B. Davis, Assignor to Eli Lilly and Co., Indianapolis, Ind. U.S. Pat. 1,438,936, May 11, 1915. Date of appl. Feb. 21, 1913.

By boiling a solution, in absolute alcohol, of pyruvic acid, vanillin, and an aromatic amine, a derivative of quinoline-1-carboxylic acid is formed having in the 2-position of the quinoline ring a *p*-hydroxy-*m*-methoxyphenyl group, and having another hydrogen of one of the CH-groups of the quinoline ring replaced by an organic radical. The position and nature of the latter are determined by the aromatic amine used, *p*-toluidine, for example, giving the 6-methylquinoline derivative. B. V. S.

*Quinoline compounds, and process of producing same.* A. B. Davis, Assignor to Eli Lilly and Co., Indianapolis, Ind. U.S. Pat. 1,438,937, May 11, 1915. Date of appl. May 20, 1914.

By condensing an ester of *p*-aminobenzoic acid, an aromatic aldehyde, and pyruvic acid, an ester of quinoline-1,6-dicarboxylic acid is produced, having the hydrogen in the 2-position replaced by an aryl group, *e.g.*, an ester of 2-phenylquinoline-1,6-dicarboxylic acid. The condensation may be effected by boiling a solution of the components in absolute alcohol. B. V. S.

*Iodine and bismuth compounds of hydroxyquinolines, their homologues, and substitution products; Preparation of—*, Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 282,453, Sept. 16, 1913.

HYDROXYQUINOLINES or their substitution products are boiled with bismuth oxydide for several hours in aqueous suspension and the precipitate is extracted with alcohol and ether. The products are highly antiseptic, combining the valuable therapeutic properties of hydroxyquinolines, bismuth, and iodine, without exerting any harmful action on the skin.—F. W. A.

*Ketones of the quinoline and isoquinoline series; Preparation of—*, A. Kaufmann. Ger. Pat. 282,457, June 20, 1913. Addition to Ger. Pat. 276,656 (see Fr. Pat. 456,251; this J., 1913, 959).

THE process described in the chief patent is also applicable to other nitriles of the quinoline and isoquinoline series in which the nitrile group in the pyridine ring is in the *ortho*-position to the nitrogen. The products, e.g., quinolyl-2- and isoquinolyl-1-alkyl ketones, are useful in the preparation of medicinal products and in perfumery.—F. W. A.

*Hypophysis; Separation of the active constituents of—*, F. Hoffmann-La Roche und Co. Ger. Pat. 282,002, Jan. 30, 1913.

THE powder obtained by triturating the extract of hypophysis (pituitary gland) or the glands themselves with sodium carbonate, is extracted with chloroform, an alcoholic solution of hydrochloric acid added, and the solution evaporated to dryness. On evaporating the aqueous extract a very small amount of a crystalline residue is obtained, which has the pharmacological action on the intestines ascribed to hypophysis extracts. The portion of the extract which affects the blood pressure and exerts the peculiar action of the extract on the uterus, is insoluble in chloroform, but may be extracted by alcohol. On evaporating the neutralised alcoholic extract to dryness, a considerable amount of a nitrogenous substance is obtained.—F. W. A.

*Oleum cedinum (oil of cedar; juniper tar oil); Separation of the constituents of—*, I. Bugarsky, L. Török, and Chinoin Gyógyszer és Vegyszeri Termékek Csevara R. T. (Kereszty und Wolf). Ger. Pat. 282,168, May 17, 1914.

MEDICINAL preparations are obtained by separating the high-boiling fractions of *Oleum cedinum* by fractional solution in methyl alcohol, with or without subsequent fractional distillation, into hydrocarbons and compounds containing oxygen. The final fraction, almost insoluble in methyl alcohol, forms on distilling over sodium a clear liquid of strong reducing properties, and of the composition,  $C_2H_4$ .—F. W. A.

*Chloroformic acid esters; Preparation of—*, A. Hochstetter. Ger. Pat. 282,131, June 21, 1913.

GOOD yields of chloroformic acid esters are obtained by the action of phosgene, dissolved in a solvent immiscible with water, on an alcohol or phenol distributed between the solvent and a layer of water in contact with it. A solvent with a suitable partition coefficient is chosen, or inert salts are dissolved in the aqueous layer, so that a considerable proportion of the alcohol or phenol is present in the layer containing the phosgene. The non-aqueous layer may be composed of the chloroformic ester which is being prepared or of liquefied phosgene.—A. S.

*Pyrazolone derivative; Preparation of a—*, I. Abelin, E. Bürgi, and M. Perelstein. Ger. Pat. 282,264, May 18, 1913.

4-DIMETHYLAMINO-1-PHENYL-2,3-DIMETHYL-5-PYRAZOLONE gives with the *o*-methylsulphonic

acid of the *p*-aminophenyl ester of salicylic acid a compound,  $C_{15}H_{14}O_4N_2S$ , which is strongly antiseptic and disinfecting, and is more effective as an anæsthetic and as a narcotic but less toxic than the original pyrazolone.—F. W. A.

*Salt of the *o*-methylsulphonic acid of the *p*-aminophenyl ester of salicylic acid; Preparation of [the hexamethylenetetramine]—*, I. Abelin, E. Bürgi, and M. Perelstein. Ger. Pat. 282,412, May 18, 1913.

HEXAMETHYLENETETRAMINE combines with the *o*-methylsulphonic acid of the *p*-aminophenyl ester of salicylic acid to form a compound,  $C_{22}H_{28}O_4N_4S$ , in which the therapeutic properties of a salol derivative and of hexamethylenetetramine are combined. The compound has higher disinfecting properties than hexamethylenetetramine, and acts as an anæsthetic without any unpleasant subsidiary effects.—F. W. A.

*Amyl acetate; Preparation of—*, Farb. vorm. Meister, Lucius, und Brüning. Ger. Pat. 282,266, Dec. 25, 1913.

THE action of aluminium amylate on acetaldehyde in amyl alcohol solution does not give ethyl acetate (compare Kremann, Monatsh. Chem., 28, 783; 29, 23), but amyl acetate and ethyl alcohol; the products can be separated by fractional distillation.—F. W. A.

*Chloral and butylochloral; Preparation of compounds of— with an acid amide*, A. Liebrecht. Ger. Pat. 282,267, Nov. 11, 1913.

A CHLORINATED aldehyde or its hydrate (1 mol.) is warmed with isovaleramide (1 mol.) in presence or absence of a solvent. The products are sedatives without having the disadvantages of chloral.—F. W. A.

*Mercurous salts of basic purines; Preparation of—*, L. Rosenthaler and A. Abelmann. Ger. Pat. 282,376, Dec. 31, 1913.

AQUEOUS solutions of mercurous salts (e.g., the nitrate) are allowed to react with basic purines, e.g., caffeine, theobromine, or theophylline, in acid (e.g., nitric acid) solution. The compounds obtained give the usual reactions of mercurous salts, and are of particular interest, as purines have been shown to prevent the harmful effect of mercury compounds.—F. W. A.

*Mercury compounds of basic purines; Preparation of—*, L. Rosenthaler and A. Abelmann. Ger. Pat. 282,377, Dec. 31, 1913.

ACID solutions of theobromine or theophylline are treated with mercuric acetate, or an aqueous suspension of theobromine or theophylline is warmed with mercuric oxide in presence or absence of alkalis. The mercury is combined in another form to that in the known N-mercury trioxypurines and the products are more stable. The theobromine compound is prepared with freshly prepared mercuric oxide in the dark, the excess of theobromine being extracted by chloroform. The compounds do not give the usual reactions of mercuric salts.—F. W. A.

*Arsenic compounds from phosphatides or substances containing them; Preparation of—*, F. Hoffmann-La Roche und Co. Ger. Pat. 282,611, March 6, 1914.

PHOSPHATIDES or substances or extracts containing them are dissolved in organic solvents and treated with arsenic acid, and the arsenic compounds thus formed are separated by methods similar to those used for the isolation of lecithin and other phosphatides. The products, which are soluble in ether, fats, and oils, and can be readily emulsified, are useful for therapeutic purposes.—A. S.

*Bacteria? Preparations for staining*—E. Beintker. Ger. Pat. 282,753, Feb. 4, 1914.

By substituting sugar or other substance capable of absorbing water for the alcohol present in the usual staining preparations, solid products are obtained from which staining solutions can be prepared as required by addition of water.—A. S.

*Preparation of water-soluble condensation products of di- and poly-hydroxybenzenes*. Ger. Pat. 282,313. See XV.

## XXI.—PHOTOGRAPHIC MATERIALS AND PROCESSES.

*Mercury compounds: Sensitiveness to light of pure*—J. M. Eder. Z. wiss. Phot., 1911, 14, 172–176. J. Chem. Soc., 1913, 108, ii, 199–200.

According to Winther (this J., 1909, 746), a solution of mercuric oxalate completely free from iron would be photochemically inactive. Experiments with carefully purified substances show, however, that the photochemical sensitiveness of solutions of mercuric oxalate (mercuric chloride and ammonium oxalate) is not dependent on the presence of traces of ferric salts, but is also exhibited by the pure mercuric compound. The decomposition of the mercuric salt is mainly determined by the ultra-violet rays, but the relative activity of the visible rays is increased if the solution contains small quantities of iron.

*Ferric salts: Sensitiveness to light of*—C. Winther and H. Oxhult-Howe. Z. wiss. Phot., 1911, 14, 196–212. J. Chem. Soc., 1915, 108, ii, 200.

SOLUTIONS of various organic salts of iron were prepared by mixing equimolar solutions of ammonium oxalate, succinate, tartrate, citrate, and acetate with measured volumes of ferric chloride solutions of varying concentration, and the mixtures were exposed to the action of monochromatic light of wave-length  $\lambda = 436, 105, 366, \text{ and } 313 \mu\mu$ . The rate at which the ferric salt is reduced remains approximately constant during the course of the reaction. For a given concentration, the sensitiveness (measured by the ratio of the amount of substance transformed to the quantity of incident radiation) increases as the absorption coefficient diminishes. It is suggested that the solutions contain at least two substances which absorb the incident rays. One of these is photochemically sensitive, and the other not, and the latter is responsible for the major part of the absorption.

*Asphalt: Colloid chemistry of*—A. Rosinger. Kolloid. Zeits., 1911, 15, 177–179. J. Chem. Soc., 1915, 108, ii, 200.

ASPHALTS which dissolve in benzene, chloroform, and hydrocarbons become insoluble in these liquids after being subjected in thin layers to the action of light. If solutions of asphalt in benzene or in a mixture of benzene and chloroform are poured on to glass plates and the solvent allowed to evaporate, the asphalt becomes insoluble even in the absence of light action. This suggests that the apparent sensitiveness of asphalt to light depends on the oxidation of the material in contact with air. In presence of sensitizers, such as safrol and eugenol, the product obtained differs from that formed in the oxidation process, and it is suggested that the action of the light in these circumstances consists in the formation of gels by adsorption of the sensitising agents in the asphalt.

*Thio-indoxyl development and its bearing on the theory of the latent image*. R. E. Crowther. Phot. J., 1915, 55, 186–197.

If thio-indoxyl is used for the development of a

photographic negative a composite image of silver and red thio-indigo is obtained, from which the silver may be removed, leaving only the colour-image (compare Homolka; this J., 1907, 487). If a plate is exposed so as to give a long range of exposures, and then developed with thio-indoxyl, reversal occurs with the colour image exactly as with the silver image, but re-reversal, or the formation of a second negative, occurs only with the silver image. If such an exposed plate is carefully watched during development with a slow developer, the formation, and subsequent disappearance, of an image, may be seen where reversal is finally obtained; in some cases, where there is a print-out image, its disappearance, or partial disappearance, may be seen. There is some variation in this latter point with different plates, some showing the first steps of the print-out image on the normal negative stage, others on the reversal stage. The author uses these facts in support of his theory of the latent image and the cause of reversal. Only a very small proportion (of the order of one molecule per grain) of the silver halide is directly affected by normal exposures, the affected part serving as starting point for the reduction of unaffected halide, and a nucleus for the deposition of silver. During exposure, halogen is split off from the silver halide and up to a certain point absorbed by the gelatin, any excess being given off from the plate. The gelatin-halogen complex so formed is decomposed by the developer with the formation of an oxidised compound and a halide. In sufficient concentration this mixture of oxidised developer and halide will convert metallic silver to the halide. Where exposure has been very prolonged the amount of gelatin-halogen complex is sufficient to determine the reaction in the opposite direction to normal development and the result is a partial or total reversal. Where exposure has been sufficiently prolonged to form a print-out image, this is partly or wholly re-converted into halide during development, the residue forming the re-reversal, or second negative stage; there is no evidence of any re-reversal except that due to the print-out image. Reversal is thus a function partly of exposure and partly of development.—R. V. S.

*Development: Acceleration and retarding of—by neutral salts*. Lippert-Gramer. Kolloid-Zeits., 1911, 15, 161–166. Z. angew. Chem., 1915, 28, Ref., 190.

THE action of a very dilute quinol developer is greatly accelerated by addition of neutral salts, such as potassium nitrate, acetate, and oxalate, and sodium sulphate and nitrite. An analogous action in the case of rapid developers, such as *p*-aminophenol, is observed only if potassium bromide has been added previously. The action of a pyrogallol developer to which bromide has been added, is retarded by addition of potassium nitrate, oxalate, or citrate. It is suggested that the accelerating action may be due to the coagulation of colloidal silver by the neutral salts, the different effect in the case of pyrogallol being explained by the fact that its oxidation products are of a colloidal nature, and hence capable of protecting colloidal silver from coagulation. The action of catechol is accelerated by potassium nitrate, but strongly retarded by potassium oxalate.—A. S.

### PATENTS.

*Colour photography*. Hudson and Keates, Ltd., London. From Frey and Salme, Zurich, Switzerland. Eng. Pat. 22,771, Nov. 19, 1914.

Is taking negatives for use in colour printing, the subject is illuminated with light of the desired colour, instead of a colour screen being used in the camera. One method is to enclose the illuminant in a case having an opening on the side next the



subject in which can be fitted a double transparent container, having a liquid filter in one compartment and a cooling liquid in the other. —B. V. S.

*Restoratives for bleached moving-picture films. Compositions for restoring the pictures on films.* F. W. Hochstetter, New York. Assignor to P. M. Pierson, Scarborough-on-the-Hudson, N.Y., U.S. Pats. 1,139,679, 1,139,683, May 18, 1915. Dates of appl. (a) Nov. 20, 1912, (b) May 27, 1913, (c) June 4, 1913, (d) and (e) Oct. 7, 1913.

(A). A MIXTURE of petrolatum, 6 oz.; spirits of camphor, 2 oz.; sulphuric ether, 0.5 oz.; and glycerin, 1 oz. (b). Fatty base, 6 oz.; camphor, 5 drms.; alcohol, 2 oz.; sulphuric ether, 0.5 oz.; and glycerin, 1 oz. (c). Oil, 6 oz.; spirits of camphor, 2 oz.; sulphuric ether, 0.5 oz.; and glycerin, 1 oz. (d). Fatty base, 6 oz., and alcohol, 2 oz. (E). Fatty base, 6 oz., and sulphuric ether, 1 oz. —B. V. S.

*Colour photography.* P. D. Brewster, East Orange, N.J., U.S.A., Eng. Pats. 3135, Feb. 10, 1914, and 2465 of 1915, date of appl., Feb. 10, 1914. Under Int. Conv., Feb. 11, 1913.

SEE Fr. Pat. 468,297 of 1911; this J., 1911, 986.

## XXII.—EXPLOSIVES; MATCHES.

*Explosion; Circumstances attending an —, which occurred on April 3, 1915, in a mixing house of the factory of Nobel's Explosives Co., Ltd., at Ardeer, Ayr.* H. Coningham, H.M. Inspector of Explosives, No. CCXIII.

THREE men were killed through the explosion of 318 lb. of thin jellies of nitroglycerin and nitro-cotton in a light wooden building, 57 ft. by 33 ft., in which were eight mixing machines. The general arrangement of the building was similar to that of the mixing house in which the explosion of Feb. 20, 1914, occurred (this J., 1914, 668). Since that accident, however, the dry nitro-cotton has been weighed in a separate building, and the main shafting for the incorporating machines is kept low down and external to the building. This had the desired effect of preventing the distribution of heavy debris, for the shaft was still in position after the explosion. Each incorporating machine had two vertical gun-metal stirring shafts, each carrying 16 blades in four sets of four, so arranged that there was about one inch between the blades when revolving, and between the ends of the blades and the bottom of the mixing pan. The pan had a jacket containing water at 60° to 62° C., and was connected by means of pipes with a barrel of water at about 65° C. The house was heated by steam radiators, and between these and the interior of the building were wire gauze screens. The explosives had been left in the warmed building overnight, and the explosion occurred when work was being started in the morning. No other building in the factory was exploded, but two expense magazines, 60 and 70 yards away respectively, were wrecked, apparently through the pressure caused by the explosion upon their roofs, rather than from its suction effect. Other buildings up to a radius of about 133 yards were also damaged. It is possible that the explosion may have been caused by a screw from the defective lid of a box falling into the jelly, but the most probable explanation is that the only lead saddle in the building may have been accidentally knocked into a mixing pan, where its contact with the stirrers generated sufficient heat to explode the contents of the pan. It is suggested that it might be possible to fill the pans with the thin jelly without the stirrers revolving, and then to start the machine and add the dope. Since the

saddle is not used while the dope is being added, the danger of starting the stirrers in a thick mass of dope and explosive would be obviated. This method of mixing is to be tried. —C. A. M.

*Explosion of nitro-cotton; Circumstances attending an —, which occurred on April 16, 1915, at the works of Coswell and Harrison, Ltd., Poyle, Middlesex.* H. Coningham, H.M. Inspector of Explosives, No. CCXIV.

TWO persons were killed and three injured as the result of an explosion of 68 lb. of dry nitro-cotton in a compartment in a building (80 ft. by 40 ft.) of corrugated iron lined with match-boarding. The other compartments comprised a store containing about 2 tons of wet nitro-cellulose, which was not connected with the explosion nor ignited by the subsequent fire, an engine and annealing room, a dynamo and mechanical shop, and stores. The dry nitro-cotton had been placed in six galvanised iron bins, 20 in. by 16 in., with removable lids, and the compartment also contained two copper granulating pans, a mixing pan, a hydro-extractor, a sifting apparatus, a cooling tank, and an incorporating mill, with a cast-iron pan and cast-iron edge runners. Only about 7 lb. of wet nitro-cotton was in the pan and no explosion had occurred in or quite close to it. The explosion may have been caused by the heat produced by friction in removing the lid from one of the bins, or a lid may have been dropped accidentally on to an open bin containing dry nitro-cotton. The presence of dry nitro-cotton in this compartment was a breach of the terms of the licence, and it is pointed out that galvanised iron bins were quite unsuitable receptacles for it. The damage done to other buildings was trifling. —C. A. M.

### PATENTS.

*Explosives.* W. Rintoul, N. Pierson, and D. H. Peacock, Stevenson, N.B., and Nobel's Explosives Co., Ltd., Glasgow. Eng. Pat. 16,692, July 13, 1914.

NITRATED furaxans of benzene, naphthalene, their homologues, and similar cyclic compounds may be used as explosives in detonators, shells, torpedo-heads, etc. Dinitrodinitrosobenzene, for example, prepared from *o*-nitroaniline by treatment with sodium hypochlorite in suspension in alcoholic potash, and subsequent nitration of the dinitrosobenzene (benzofuroxan) thus formed, is suitable for use in detonators to replace part of the mercury fulminate, and in other cases where tetranitroaniline, trinitrotoluene, etc., are used. The salt-like compounds formed from nitro-furaxans and potash, soda, etc., may be used in complete substitution for mercury fulminate. Two formulae are given for the preparation of blasting explosives, one containing 9% dinitrobenzofuroxan, together with potassium perchlorate (42.8%), nitroglycerin (31.5%), a liquid nitro-compound such as nitrotoluene (13.5%), nitro-cotton (1%), and wood-meal (2.2%); the other containing 20% dinitrobenzofuroxan and 80% ammonium nitrate. —B. V. S.

*Explosive.* G. Burgschmiet, Morden, Canada. U.S. Pat. 1,139,339, May 11, 1915. Date of appl., Jan. 12, 1914.

A MIXTURE of about 80% of ammonium nitrate, 18% of dinitrotoluene, and 2% of charcoal and wood meal. —C. A. M.

*Match-heads; Composition for —.* W. C. Pierson, Cleveland, Ohio. U.S. Pat. 1,138,146, May 4, 1915. Date of appl., Oct. 28, 1912.

THE composition contains nitrocellulose or other nitrated carbohydrate, a metallic nitrate, potassium chlorate, potassium dichromate, plaster of Paris, powdered glass, and glue. —C. A. M.

## XXIII.—ANALYTICAL PROCESSES.

**Iron:** Volumetric determination of — in hydrochloric acid solution by the bichromate method, using diphenylcarbohydrazide as indicator. L. Brandt. *Z. anal. Chem.*, 1914, **53**, 729—745. *J. Chem. Soc.*, 1915, **108**, ii., 285.

IN the method described previously by the author (this J., 1914, 41) sulphuric acid alone may be used in place of the manganese solution containing sulphuric and phosphoric acids. Arsenic, if present, must be oxidised previous to the titration of the iron. The correction for the amount of bichromate consumed by the indicator is quite small; it cannot be determined by a control titration of the indicator itself, but if this titration is made and a second quantity of the indicator added and titrated, the amount of bichromate used in the second titration will approximate to that used by the indicator in the titration of the iron.

**Selenium:** Gravimetric determination of —. A. Gutbier and F. Engeroff. *Z. anal. Chem.*, 1915, **54**, 193—205.

SELENIUM dioxide is reduced quantitatively to selenium by hydrazine sulphate, or hydrazine hydrate, in dilute nitric acid solution; the hydrazine solution should be added to the cold selenium dioxide solution and the mixture then heated gradually. In this way, there is no danger of the spray formed by the escaping nitrogen carrying off finely-divided selenium (see Meyer, this J., 1911, 335). The nitric acid solution containing the selenium dioxide may be evaporated to dryness without loss of selenium, but a small loss occurs when the residue is heated further for 1 hour. —W. P. S.

**Palladium and tin:** Separation of — by means of dimethylglyoxime. A. Gutbier and C. Fellner. *Z. anal. Chem.*, 1915, **54**, 205—208.

PALLADIUM is precipitated by dimethylglyoxime from acid solutions whilst tin remains dissolved. 150 c.c. of the solution, containing hydrochloric acid but no free chlorine, is heated on a water-bath, and treated with a 1% dimethylglyoxime solution until a turbidity is no longer produced. Heating is continued for 1 hour more, the mixture is cooled, the precipitate collected on a filter, washed with dilute (not more than 2%) hydrochloric acid, and ignited at first in contact with air and then in an atmosphere of hydrogen. The tin may be determined in the filtrate. —W. P. S.

**Palladium from tin:** Separation of — by electrolytic deposition of the palladium. A. Gutbier, C. Fellner, and R. Emslander. *Z. anal. Chem.*, 1915, **54**, 208—213.

A SOLUTION containing the two metals is poured into a mixture of 25 c.c. of 2N-sulphuric acid and 500 c.c. of water; after some time, the mixture is heated to 65° C. and submitted to electrolysis at this temperature. A current of 1.25 volt and 0.25 ampere is employed; the cathode consists of a semi-circular piece of platinum gauze and the anode of a platinum spiral. The electrolyte is stirred by a glass screw rotated between the electrodes at 2500 revolutions per minute. After the palladium has been deposited, the solution is boiled, with addition of ammonium nitrate, and the tin oxide is collected. (See also Anders, this J., 1904, 667; Wöhler and Sprengel, 1911, 386.) —W. P. S.

**Phosphorus:** Determination of lipid and acid-soluble — in small amounts of serum. I. Greenwald. *J. Biol. Chem.*, 1915, **21**, 29—36.

ONE c.c. of the serum is diluted to 10 c.c. with a solution containing 1% each of acetic acid and picric

acid, and after two hours the mixture is filtered. The filtrate is evaporated to 1 c.c., heated with 1 c.c. of sulphuric acid until all picric acid has been expelled, and the oxidation then completed by the addition of nitric acid and further heating. The solution is diluted to a definite volume and aliquot portions are mixed with nitric acid, diluted, and treated with 2 c.c. of molybdic acid-strychnine reagent. The coloration obtained is compared with that produced by known quantities of phosphoric acid. The residue remaining on the filter is also oxidised with sulphuric and nitric acids and the phosphoric acid determined in a similar way. The reagent is prepared by dissolving 95 grms. of molybdic acid and 30 grms. of sodium carbonate in 600 c.c. of warm water, cooling, adding 141 c.c. of concentrated nitric acid, and diluting to 1 litre; 10 c.c. of this solution is mixed with 1 c.c. of a 2% strychnine sulphate solution and the mixture is used immediately. The amount of phosphorus not precipitated by the acetic acid-picric acid mixture usually varies between 2 and 6 mgrms. per 100 c.c. of serum. The lipid phosphorus lies between 5 and 15 mgrms. —W. P. S.

**Blood:** Chemical detection of —. D. Gausmini. *Boll. Chim. Farm.*, 1914, **53**, 777—781. *J. Chem. Soc.*, 1915, **108**, ii., 295.

THE author has investigated Baccelli's test for blood (*Arch. Int. Med. Legale*, 1913, **4**, 163), which is carried out as follows. Two c.c. of an aqueous alizarin-S-blue solution diluted to a mahogany-yellow colour is mixed with about one-half the volume of 3% hydrogen peroxide solution. A little of the liquid to be tested is then poured slowly down the wall of the test-tube. If blood is present, gentle shaking rapidly renders the liquid intensely blue, the blue colour slowly fading and giving place to a red colour, which is moderately stable. This reaction is stated to give a positive result with 1 part of blood in 20,000, and to answer well with blood which has undergone alteration and become insoluble in water, the blood being then first dissolved in alcohol acidified with hydrochloric acid.

**Blood:** Determination of non-protein nitrogen in —. I. Greenwald. *J. Biol. Chem.*, 1915, **21**, 61—68.

THE blood is diluted to 10 times its volume with a 2.5% solution of trichloroacetic acid and the mixture is filtered after 30 minutes. The lipids are precipitated completely with the proteins, and added amino-acids may be recovered in the filtrate; the latter may contain a small quantity of protein which can be removed by shaking with kaolin. This filtrate contains all the soluble, non-protein constituents of the blood. The normal non-protein nitrogen appears to be amount of non-protein nitrogen appears to be amount of 30 mgrms. per 100 c.c. of blood. Methyl alcohol cannot be used as a precipitant for the proteins since it is not a good solvent for certain amino-acids, and at the same time it dissolves a quantity of lipid. —W. P. S.

**Colloids:** Measurement of the protective action of proteolite —. J. Grob. *Z. physik. Chem.*, 1914, **88**, 411—418. *J. Chem. Soc.*, 1915, **108**, ii., 239.

THE rates of decomposition of hydrogen peroxide by colloidal platinum with and without the addition of a protecting colloid were determined. The following results were obtained for the action of gelatin: unprotected colloid decomposed 50% of the hydrogen peroxide in thirty minutes, and addition of 0.001% gelatin increased the time to 131 minutes; 0.01% gelatin, 138 minutes; 0.05% gelatin, 186 minutes; and 0.10% gelatin, 295 minutes. In alkaline solution the protective

action was not so marked, the rate of decomposition being reduced only about one-third. Comparative measurements were made of the protective action of gelatin, gum arabic, and dextrin. The order of protective action was that given above, and it persisted for all concentrations from 0.1% to 0.0001%, the relative values being approximately the same as those found by Zsigmondy by means of the gold numbers.

*Analysis of lactic acid.* Balderston. See VII.

*Determination of sulphuric acid and potassium, especially in potash salts.* Vaubel. See VII.

*Blue and red Congo dyes. Theory of indicators.* Hantzsch. See IV.

*Isomerides of helianthins and aminoazobenzene salts.* Hantzsch. See IV.

*Concentration method for the determination of small quantities of phosphoric acid in limestone.* Hinden. See VII.

*Determination of carbon dioxide in minerals.* Borgström. See VII.

*Determination of arsenic in lead by hypophosphorous acid.* Brandt. See X.

*Separation of arsenic from tungsten [vanadium, and molybdenum].* Dieckmann and Hilpert. See X.

*Practical testing of working cyanide solutions.* Croghan. See X.

*Detection of phytosterol in animal fats by precipitation with digitonin.* Kühn and Wewerinke. See XII.

*Separation of dihydroxy- and tetrahydroxystearic acid.* Matthes and Rath. See XII.

*Approximate determination of non-volatile unsaponifiable substances in linseed oil varnish.* Bárány. See XIII.

*Determination of bitumen in rubber mixings.* Porritt and Anderson. See XIV.

*Use of nitric acid as a solvent for compounded and vulcanised rubbers.* Jones. See XIV.

*Determination of small amounts of carbon dioxide [in rubber goods] in presence of sulphides.* Jones. See XIV.

*Determination of mineral matter in vulcanised rubber.* Jones. See XIV.

*Determination of mineral matter in rubber mixings.* Porritt and Wheatley. See XIV.

*Biological detection and valuation of tannins.* Kobert. See XV.

*Determination of the sulphur-transforming power of soils.* Brown and Kellog. See XVI.

*Determination of manganese in soils.* von Horváth. See XVI.

*Vegetation experiments and soil analysis.* Lemmermann. See XVI.

*Determination of phosphoric acid in soil extracts.* Den Berger. See XVI.

*Iodometric determination of phosphoric acid in vegetable products and soils.* Preisinger and Frodl. See XVI.

*Use of sodium citrate for the determination of reverted phosphoric acid.* Bosworth. See XVI.

*Effect of clarification with lead acetate and tannin in the polarimetric examination of sugar, dextrin, and starch solutions.* Grossfeld. See XVII.

*Composition and effects of lupin seeds [due to enzymes]. [Detection of lupin seeds in admixture with castor oil seeds.* Muenk. See XIXA.

*Determination of tartaric acid in beverages, especially in wines.* Häussler. See XVIIII.

*Alcohol reaction of milk.* Auzinger. See XIXA.

*Determination of lecithin in milk.* Brodrick-Pittard. See XIXA.

*Cause of acidity of fresh milk of cows, and a method for the determination of acidity.* Van Slyke and Bosworth. See XIXA.

*Determination of dissolved oxygen in water.* Winkler. See XIXB.

*Determination of the reducing power of natural waters.* Winkler. See XIXB.

*Transformation of antipyrine into dianitpyrime-methane. [Detection of antipyrine in pyramdone.]* Astre. See XX.

*Determination of citral in concentrated oil of lemon.* Böcker. See XX.

*Reactions of vanillin.* Häussler. See XX.

*Analysis of ethyl acetate.* Szeberényi. See XX.

#### PATENT.

*Apparatus for taking samples of liquids contained in receptacles.* Ger. Pat. 282,172. See I.

### XXIV.—MISCELLANEOUS ABSTRACTS.

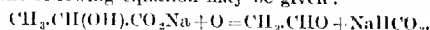
*Metals and oxides; Emissivity of—.* II. Measurements with the micropyrometer. G. K. Burgess and R. G. Waltenberg. Bull. Bureau of Standards (U.S.A.), 1914, 11, 591-605.

The monochromatic emissivity of various metals and oxides may be rapidly determined, both in the solid and liquid states, by means of the micropyrometer (this J., 1913, 162) between 900° and 3000° C. The results are accurate to about 1% and may be obtained with as little as 0.01 mgrm. of the substance. Platinum is taken as the standard substance and tables of measurements are given, chiefly for red and green light of wavelengths 0.650  $\mu$  and 0.517  $\mu$ , of the emissivity of 23 metals in hydrogen and 12 oxides in air. Most solid metals showed a practically negligible temperature coefficient of emission between 20° C. and the m. pt. Nickel oxide showed a negative coefficient. The discontinuity in emissivity for  $\lambda = 0.650 \mu$  at the m. pt. was marked in the cases of gold, copper, and silver, and was appreciable for platinum and palladium. The emissivity characteristic of liquid palladium may persist for a time after solidification. The increase in red brightness when platinum melts amounts to about 15%; it therefore appears that the Vielle unit of light, depending upon the luminous radiation from the surface of platinum at its m. pt., cannot be regarded as a definite standard. — J. R.

*Alkali carbonates; Formation of from neutral salts in the light.* Biochemistry of the action of rays. III. C. Neuberg and W. H. Peterson. Biochem. Zeits., 1914, 67, 63-70. J. Chem. Soc., 1915, 108, i, 212.

WHEN sterilised solutions of potassium malate, succinate, citrate, or lactate or potassium sodium tartrate were exposed to light and air in the

presence of a catalyst, such as ferrous, ferric, uranyl, or manganous sulphate, or sodium anthraquinone-2,7-disulphonate, or 9,10-dichloroanthracene-2,7-disulphonate, an increase in the alkalinity of the solution was observed. As an example of the method of formation of the alkali, the following equation may be given:



## Trade Report.

### Contraband of war.

A ROYAL Proclamation, dated May 27th, 1915, declares that "Tolmol, and mixtures of tolhol, whether derived from coal-tar, petroleum, or any other source, will be treated as absolute contraband." Also that in the Proclamation of Dec. 23rd (see this J., 1914, 1230), the words "all other metallic acetates" (after "calcium acetate") shall be omitted, and that linseed oil will be treated as conditional contraband.

### Prohibited exports.

By an Order in Council dated June 2nd, 1915, the exportation of the following goods is prohibited to all destinations abroad other than British Possessions and Protectorates:—Hydrochloric acid, oxides and salts of nickel, oxides and salts of tungsten; mineral and vegetable wax, ground nuts, earth nuts, or pea nuts (*Arachides*), hempseed, palm nuts and palm kernels, poppy seed, rape or colza seed, sunflower seed; tungsten filaments for electric lamps. Among the articles added to the list of goods the exportation of which is prohibited to all foreign ports in Europe and on the Mediterranean and Black Seas, other than those of France, Russia (except Baltic ports), Spain, and Portugal, are arsenic and its compounds, ground nut or earth nut cake and meal, hempseed cake and meal, husk meal, locust bean meal, meat meal, palmnut cake and meal, poppyseed cake and meal, rapeseed or colza seed cake and meal, sesame seed cake and meal, soya bean cake and meal, sunflower seed cake and meal.

### Prohibited exports.

AUSTRIA-HUNGARY.—According to a decree of May 8th the following articles have been added to the list of prohibited exports: Ammonia, chloral hydrate, diomine, digalen, menthol, perhydrol, pepperment oil, pilocarpine, ipseacanthia, liquorice-root, rhubarb, valerian-root, salicylic acid and its salts, tannalbin, theobromine and its derivatives, and hexamethylenetetramine.

GERMANY. According to a decree of the Imperial Chancellor, dated May 20th, the exportation of wood-vinegar (crude acetic acid), oil-varnishes, spirit-varnishes, and shellac-preparations is prohibited. The prohibition of the exportation of natural magnesium carbonate (magnesite) has been revoked.

## Books Received.

THE CHEMISTS' YEAR BOOK, 1915. Edited by F. W. AYACK, M.Sc., Tech. In two vols. Sherratt and Hughes, 31, Cross Street, Manchester. 911 pages. 6½ x 4 in. Price 10s. 6d.

ADVANTAGE has been taken of the cessation of the supply of the German pocket-books and annals, to produce a similar work in the English language, which it is intended to revise each year. The Editor is to be congratulated on the results of his labours, which should form a most useful addition

to the chemists' library. The first volume contains a calendar for the year and a large number of analytical notes, conversion tables, logarithms, and mathematical constants. The second volume includes tables of physical constants of elements, their compounds, and various solutions, together with notes on mineralogy and a large range of chemical-technological subjects.

THE LEATHER TRADES' YEAR BOOK, 1915. Edited by M. C. LAMB and J. GORDON PARKER. The Anglo-American Technical Co., 112, Tower Bridge Road, London, S.E. 212 pages. 9 x 6 in.

THIS Year-Book is the official organ of the United Tanners' Federations of Great Britain and Ireland. The first part of the book is devoted to information concerning the various Federations, and to statistical and other matters of interest to the tanner and leather chemist. The remainder of the book is occupied by an interesting series of papers on a variety of subjects pertaining to the industry; these include contributions by such authorities as H. R. Procter, E. Niboul, J. T. Wood, and M. C. Lamb.

POTASH SALTS AND OTHER SALINES IN THE GREAT BASIN REGION. By G. J. YOUNG. U.S. Dept. of Agriculture, Bulletin No. 61. Government Printing Office, Washington. 92 pages. 9½ x 6 in. Price 15 c.

THIS Bulletin embodies the results of investigations carried out in co-operation with the U.S. Geological Survey and the Mackay School of Mines, Reno, Nev., to determine the sources of potash in the basin region. The area under consideration covers practically the whole of Nevada, the southern part of Oregon, the western part of Utah, and certain parts of eastern and south-eastern California. The chief result of the investigations is to show that, of the basins examined, Searles Lake is the only one where the concentration of potassium in the residual brims is sufficient to offer prospects of commercial success.

## \* New Books.

(The Roman numerals in thick type refer to the similar classification of abstracts under "Journal and Patent Literature" and in the "List of Patent Applications.")

VII. *Diggs*, S. H.: Influence of the concentration of potassium iodide on the rate of diffusion of iodine in potassium iodide solution. (Charlottesville, Va., Univ. of Va. 1914. 477-512 p. tabs. Q. 1915. Pap. 50 c.

X. *Backert*, A. O.: Ed. The A B C of iron and steel; with a directory of the iron and steel works and their products of the United States and Canada. (Cleveland, O., Penton Pub. Co. 154-338 p. II. pers. plans fold. pls. tabs. diagrs. 11". 1915. \$5.

*Doelter*, C.: Handbuch d. Mineralchemie. III. Bd. 6. u. 7. Abtlg. Dresd., Steinkopff. 1915. Each Abtlg. M. 6.50.

*Lyon*, D. A., and *Keeney*, R. M.: The smelting of copper ores in the electric furnace. Wash. D.C. Gov. Pr. Off. 80 pp. II. 8vo. (Bu. of Mines. Bull. 81). 1915.

*McFarren*, H. W.: Practical stamp-milling and amalgamation. 3rd ed. with a chapter on arrangement and construction costs of stamp-mills. By C. T. Hutchinson. San Francisco. Mining and Scientific Press. C. 1911. 231 pp. II. 8vo. \$2.

*Fulham Process Co.*: A text book on welding and cutting metals by the oxy-acetylene process; with 64 illustrations. 3rd ed., rev. Minneapolis. c. 7-134 p. 8vo. 1915. \$1.50.

**White, C. H.:** Methods in metallurgical analysis. 166 illustrations. N.Y., Van Nostrand, c. 9 + 356 p. (3½ p. bibl.) D. 1915. \$2.10 n.

**XII. Ingle, H.:** Manual of oils, resins, and paints, for students and practical men. In three vols., each volume complete in itself and sold separately. Vol. I, Analysis and valuation. With diagrams by the Author and J. A. L. Sutcliffe. Cr. 8vo. Griffin and Co. London, 1915. Net 3s. 6d.

**XIII. Underwood, N., and Sullivan, T. V.:** Chemistry and technology of printing inks. N.Y., Van Nostrand, c. 139 p. il. O. 1915. 83 n.

**XIV. Lock, R. H.:** Rubber and rubber planting. (N.Y., Putnam, 1911. 11 + 215 p. il. pls. 12mo. 1915. \$1.50 n.)

**XV. Stieckelberger, E.:** Versuch e. Geschichte der Gerberei. 65 S. m. z. Tl. eingeklebten Abbildgn. 8vo. Berlin, Springer, 1915. M. 8.

**XVII. Pages, G.:** Le sucre et l'utilisation de ses sous-produits à la ferme, fig. (VIII.—88 p.) in-16, cart. Hachette, Paris, 1915. Fr. 1.50.

**XVIII. Brauer, H.:** Malz-Fabriken, Bremerien, Spirit- u. Presshefen-Fabriken; Die deutschen, in Besitze v. Aktien-Gesellschaften. Jahres-Bericht der finanziellen Verhältnisse u. Betriebsergebnisse im Geschäftsj. 1913/14. (Einfbl.: 1915) 18. vollständig umgearb. u. verm. Aufl. (N. 396 S.) gr. 8. Berlin, Verlag f. Börsen- u. Finanzliteratur, 1915. Geb. in Leinw. M. 6.

**Kroners, E.:** Agricultural alcohol: studies of its manufacture in Germany. Wash. D.C., Gov. Pr. Off. 36 p. tab. 8vo. (Dept. of Agric. Bull. No. 182). 1915.

**XIXA. Hart, R. N.:** Leavening agents: yeast, leaven, soft-riasing fermentation, baking powder, aerated bread, milk powder. Easton, Pa., Chemical Pub. c. 90 p. il. 8vo. (1915. 81. *Daire:* Les microbes dans l'industrie laitière, 20 fig. (121 p.) in-18. Baillière, Paris. 1915. Fr. 1.50.

**Merrill, E.:** Production and consumption of dairy products. (Wash. D.C. Gov. Pr. Off.) 19 p. tab. 8vo. (Dept. of Agric. Bull. No. 177). 1915.

**Tedesco, G.:** Trattato di chimica applicata alla bromatologia e alla igiene. La ediz. Terni. 16. p. 1109. XXIV. 1915. Lire 12.

**XIXB. Elwell, W. B., and Grissom, J. T.:** Preparation of nicotine extracts on the farm. Blacksburg, Va. (Agricultural Experiment Station). 1914. 16 p. il. 8vo. (Bulletin).

**Löffmann, H.:** Examination of water for sanitary and technical purposes. 7th ed. rev. and enl. Phil. Blakiston, c. 16 + 110 p. il. 12mo. 1915. 81.25 n.

**Mathews, E. R.:** Refuse disposal. A practical manual for municipal engineers, members of local authorities, etc. With 8 detailed drawings, and 91 illustrations in the text. Cr. 8vo. Charles Griffin and Co. London, 1915. Net 6s.

**XX. Askinson, G. W.:** Perfumes and cosmetics: their preparation and manufacture. Tr. from the German. Rev. with additions by W. S. Dudley and a corps of experts. II. by 32 engravings. 11th ed. N.Y., Henley, c. 1892—1915. 19 + 311 p. O. 1915. 85.

**XXIII. Peters, F.:** Handb. d. analyt. Chemie. 3. Lfg. Hdbg. Carl Winter. 1915. M. 2.

**XXIV. Bauer, Dr. H.:** Geschichte der Chemie. II. Von Lavoisier bis zur Gegenwart. 2. verb. Aufl. (410 S.) 1915. 8. Berlin. G. J. Göschen. M. 1.

**Blücher, H.:** Auskunftsbuch f. die chemische Industrie. 9. verb. u. stark verm. Aufl. (XVI. 1159 u. 13 S.) gr. 8. Leipzig. Veit & Co. 1915. Cloth. M. 18.

**Chamot, K. M.:** Elementary chemical microscopy. N.Y., Wiley, c. 6 + 410 p. figs. 8. 1915. \$3 n.

**Firth, J. B.:** Practical physical chemistry. Cr. 8vo. pp. 190. Methuen. 1915. 2s. 6d.

**Gmelin u. Kraut's anorgan. Chemie.** 7. Aufl. v. Friedheim u. Peters. 182—184. Lfg. Hdbg., Carl Winter. 1915. Each Lfg. M. 1.80.

**Industrial Chemistry:** A manual for the student and manufacturer. Edited by A. Rogers. 2nd ed., thoroughly revised and enlarged. Roy. 8vo. pp. 1026. Constable, London. 1915. Net 24s.

**Perkin, F. M., and Jagers, E. M.:** Text-book of elementary chemistry. Cr. 8vo. pp. 311. Constable, London. 1915. Net 3s.

### \* Dissertations.

**Siebert, G. A.:** Ueber o-Aminobenzolmercaptan und o-Phenolmercaptan. Marburg i. H. 1914. 77 S. 8.

**Smith, S.:** Ueber 1-methyl-2-amino-1-äthanoyl-cyclohexan. Ueber die Ozonide des  $\Delta^3$ -p. Mentheins. Kiel. 1914. 36 S. 8.

**XXIII. Berceis, B.:** Bestimmungen der spezifischen Wärme unvollkommener Gase nach der Durchströmungsmethode. Heidelberg. 1911. 83 S. m. 1 Tafel.

**XXIV. Krüger, E.:** Zum Molekularzustand von Flüssigkeiten und Lösungen. Leipzig. 1911. 82 S. 8.

**Nordenson, H.:** Ueber die Bedeutung des Lichtes für die Bildung und Stabilität kolloider Lösungen. Epsala. 1911. 111, 161 S. m. 11 (10 Kurven) Taf. gr. 8.

**Hultslein, A.:** Beiträge zur Kenntnis des  $\alpha$ -Terpinols,  $\beta$ -Terpinols und des  $\Delta^1$ -Menthens. Göttingen 1913. VI, 53 S. 8.

**Herz, A.:** Ueber komplexe Eisenverbindungen der Benzoesäure und der Salicylsäure. Tübingen 1911. 92 S. 8.

**Imannsdorfer, E.:** Synthese einiger alkylsubstituierter Hippurylmalester und ihre Kondensation zu Pyridinderivaten. Berlin 1914. 38 S. 8.

**Ischick, A.:** Ueber die Hydrierung von Chinalkaloiden und Chinaketonen. Jena 1913. 38 S. 8.

**Jahn, F.:** Ueber Jodosbenzoesäure. Leipzig 1914. 28 S. 8.

**Memminger, K.:** Ueber das Einwirken von Brom auf Azo-Acetessigester, Azo-Isoxazolone und Azo-Pyrazolone. Tübingen 1911. 71 S. 8.

**Oettingen, W. F. v.:** Die Hydrierung des Santonins zu stereoisomeren Santoninen und andere Reduktionsversuche in der Santoninreihe. Göttingen 1913. 74 S. 8.

**Perci, E.:** Camarine aus Propionyllessigester. Berlin T. H. 1913. 32 S. 8.

**Raue, H.:** Ueber neue Oxydations- und Spaltprodukte des Brucins. Berlin 1911. 11 S. 8.

**Schäfer, A.:** Ueber einige Derivate des 1-Phenyl-3-Methyl-5-Iminopyrazolons. Rostock. 1913. 69 S. 8.

**Schmidt, J.:** Ueber einige Derivate des Methylisoxanolidhydrates. München Techn. Hochschule 1913. 46 S. 8.

**Schwarz, K. R.:** Beiträge zur Kenntnis der Oxydationsvorgänge. Ueber das Dicyklopentadien. München 1913. 59 S. 8.

\* Compiled by H. Grevel and Co., 33, King Street, Covent Garden, London, W.C., from whom all the works in the preceding list can be obtained.











